



BOOK OF ABSTRACTS

Welcome to the event XXI Brazilian Symposium on Theoretical Chemistry

The **XXI edition of the Brazilian Symposium on Theoretical Chemistry (SBQT)** will mark the 40th anniversary of the largest meeting in Theoretical and Computational Chemistry in Brazil and will take place, for the first time, in a totally virtual format.

Keeping with tradition, this edition will have a very diversified program, contemplating different research lines existing in the country, including quantum mechanics, Statistical Mechanics, molecular modeling, liquids, solids and interfaces, gas phase reactions, development of algorithms, among others and encompassing numerous applications.

Our meeting remains a unique opportunity to promote, disseminate, create collaborations, and share knowledge and advances in Theoretical and Computational Chemistry in Brazil, in addition to strengthening the relations with experimentalists. The program will have lectures, oral communications, round tables, and poster sections, with Brazilian and foreign speakers.

We welcome you all!

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NOTA EXPLICATIVA

Os resumos do SBQT 2021 foram baixados diretamente do site do evento (<https://eventos.galoa.com.br/sbqt-2021/page/727-home>) em dezembro de 2023 por meio de um *bot* escrito em Python. O programa foi desenvolvido pelo doutorando do Programa de Pós Graduação em Engenharia de Defesa (PGED) do Instituto Militar de Engenharia (IME) Rubens Caio de Souza.

Os seguintes resumos não puderam ser baixados pois os respectivos links estavam quebrados:

- Validação de esquemas de otimização para o desenvolvimento de método composto em cálculos de entalpias de formação;
- Estudo QSAR de derivados do honokiol com atividade antitumoral;
- LQTA Grid Hull and LQTAGrid for 4D-QSAR Descriptors calculation: a comparative study;
- Receptor-dependent and independent LQTA-QSAR studies with a set of 5-HT2AR inhibitors.

Para qualquer acréscimo ou correção a este documento, basta entrar contato.

Aproveitem para conhecer o melhor da Química Teórica Brasileira em 2021!

Cordialmente,

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Isothermal adsorption of polyelectrolytes on charged nanopatterned surfaces

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Key words: Monte Carlo simulation; polyelectrolytes; nano-patterned surfaces

In the current study we have investigated, using Monte Carlo simulations, the adsorption of polyelectrolytes on the charged nanopatterned surfaces. Different surface's patterns were considered and we noticed that the amount of adsorption is directly dependent on the size of the domains.

It is well known that theoretical study of adsorption of charged particles on charged plates is not an easy task since mean-field approximation collapses to describe their behavior in high correlated regions [1-2]. Nevertheless, there are some approximations using simple models, such as, one component plasma near a neutralizing background and some similar theories which work well in regions of high electrostatic correlations [2-3]. The situation gets worse when surfaces are not homogeneously charged or some nanopatterns exist on them. However, always one of the best ways to study these systems is computational simulations.

Recently, an efficient and robust method has been introduced to simulate nanopatterned charged surfaces inside an electrolyte solution [4]. In the mentioned method, to deal with the long-range Coulomb interaction between the ions a modified 3d Ewald summation method was used [5-6]. The surfaces are considered as periodic charged sinusoidal patterns. The analytical solution of the Poisson equation was evaluated in order to properly consider the effect of the nanostructured charged walls as an external potential.

We showed that, polyelectrolytes are adsorbed to domains with opposite charge and concentrated to the center of the domains where there is higher charge density. By studying the average distance of head to tail of molecules we observed that the molecules prefer to become extended on the surface for stripes configurations where the plate has transnational symmetry in one direction, this can be seen in Fig. 1.

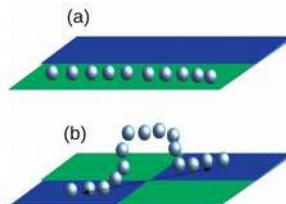


Fig.1. Representation of different configuration of polymer on the patterned surface a) stripe pattern, b) Checkerboard pattern

Also, it was observed that the amount of adsorption may relate to the head to tail distance of molecule in bulk. For checkerboard configurations, when the edge of the domain becomes comparable with this significance distance (head to tail distance) the adsorption decreases for the same scaling variable which is directly proportional to surface charge density. However for longer polyelectrolytes since they can have a bend configurations along the diagonal of square domains and still have some segments near the opposite charged domains, they can find a more stable configuration and reach to the center of others opposite neighbor charged domains via diagonal path and as a result it can be seen that adsorption increases by reducing the size of domains [7].

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Structure-activity relationships (SARs) of novel tri-substituted thiazole derivatives with antimicrobial activity

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Palavras-Chave: DFT, Structure-activity relationships, antimicrobial.

INTRODUCTION

Recently, a dramatic worldwide increase of severe infections by only cause of microbes and microorganism resistance to multiple antibacterial and antifungal agents have become a serious problem. Based on the above facts, considerable interest has been devoted to discovering new lead structures and novel chemical entities, which will act as antimicrobials.[1] In particular, theoretical predictions about the electronic structure of chemical compounds play a fundamental role in the mechanism associated with pharmacological activities.[2] In this study, the combined experimental and theoretical analysis of unknown tri-substituted thiazole derivatives is presented to evaluate their antimicrobial assay.

METHODOLOGY

Theoretical investigation of the thiazole derivatives (**Fig. 1**) was carried out in the framework of Density Functional Theory (DFT) calculations applying B3LYP hybrid functional and 6-31+G(d,p) basis set, implemented on GAMESS-US program package.[3]

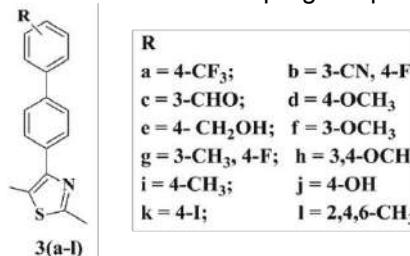


Figure 1. Chemical structure of investigated tri-substituted thiazole derivatives.

RESULTS AND DISCUSSIONS

Table 1 summarized the theoretical electronic parameters for investigating the thiazole derivatives. In all the compounds, it was observed that there was no much difference in HOMO energy of all the compounds, even though compounds have different substituents. However, the LUMO orbital energies were affected by electron donation or withdrawing groups on the structure; consequently, there was a change of energy according to the attached groups. Among the investigated parameters, the relation

between biological activity and LUMO orbital energy displayed a piece of clear evidence for the identification of excellent to low biological active compounds.

Table 1. Theoretical results of compounds 3(a-l).

Compound	HOMO (eV)	LUMO (eV)	E _{gap} (eV)
3a	-5.99	-1.42	4.57
3b	-6.10	-1.79	4.30
3c	-5.91	-1.87	4.04
3d	-5.43	-1.02	4.41
3e	-5.58	-1.05	4.52
3f	-5.62	-1.06	4.56
3g	-5.72	-1.16	4.56
3h	-5.42	-1.03	4.39
3i	-5.58	-1.05	4.53
3j	-5.49	-1.07	4.45
3k	-5.79	-1.35	4.44
3l	-5.83	-0.95	4.88

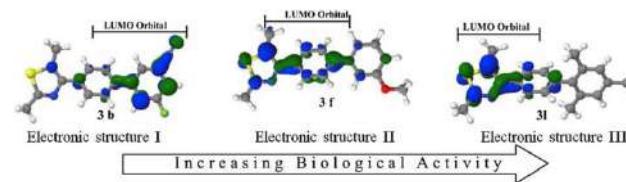


Figure 2. LUMO orbital of lowest, moderate and excessive biological activity compounds 3b, 3f, and 3l by DFT/B3LYP calculations.

CONCLUSIONS

A series of biologically active tri-substituted thiazole derivatives were analyzed for their antimicrobial activity. Theoretical calculations evidenced the role of LUMO energy and localization for enhanced biological activity.

ACKNOWLEDGEMENTS

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Rate processes on the verge of the thermodynamic and the kinetic limits

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Palavras-Chave: *Transitivity, non-Arrhenius, Scaling plane.*

The phenomenological information from both laboratory experiments and computational simulations are enlarging our understanding of the temperature dependence of rates of chemical transformations and transport phenomena at low temperatures: there, deviations from linearity of Arrhenius plots are ubiquitous. Our statistical mechanics approach evaluates the effect of temperature on chemical reaction rates in cold environments using venerable mathematical concepts arising from “criteria for choices”: Bernoulli-like urn distribution and Euler's formula for the exponential as limit of a succession for events, corresponding in statistics to the Pareto-Tsallis statistical weights.

From statistical mechanics perspectives¹, the transitivity concept was introduced as a measure which regulates transit in physicochemical transformations, not necessarily involving reference to transition-state hypothesis of Eyring. The *Transitivity plot* is defined as the reciprocal of the apparent activation energy vs reciprocal absolute temperature² which permits a representation of non-Arrhenius behavior in a “geometrical scale” and makes explicit a positive or negative linear dependence of transitivity γ for several deviation cases. The information presented here accounts for a systematization of the foundations and tools developed over the last ten years³ to handle the kinetics of non-Arrhenius processes. Below applications will be documented in a variety of contexts:

i) Ranges of universality are observed analyzing transport properties data of glass-forming liquids in an appropriate scaling kinetic plane⁵, *the transitivity plot*, on approaching glass transition temperature T_g . In both two examples presented in Fig. 1, T^* marks a slope change, for temperature larger vs lower than T^* , fragile vs moderately strong behaviors are identified. It is remarkable to note in Fig. 1 that in the temperature ranges above and below T^* , the Aquilanti-Mundim propensity of transitivity with β exhibits aspects of universality.

ii) The rates of biological processes are strongly affected at low temperatures by deviations from Arrhenius law; however there are large uncertainties especially when quantifying, the deviations using the “Arrhenius Break Temperature” assumption⁶. The

difficulty of identifying a transition temperature in the Arrhenius plot⁷ can be overcome using the transitivity plot, emphasizing sudden transitions described within the Aquilanti-Mundim law.

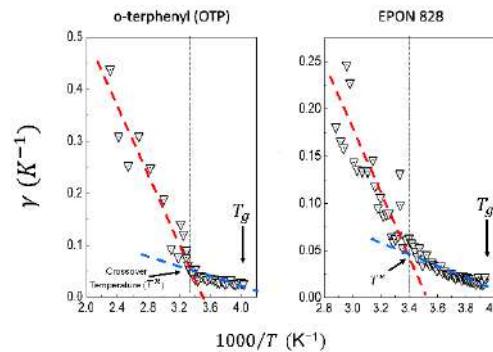


Fig1: Transitivity plot displaying the crossover between two distinct ranges of validity of Aquilanti Mundim for o-terphenyl, EPON 828. Note the crossover temperature denoted by T^* marks the change of fragile to moderately strong behavior

iii) Hypergeometrically-based fits are provided. It was recognized the similarity between the functional form of transitivity with respect to the rate coefficient and the reciprocal temperature; and the *renormalization group equation and coupling parameter* named after Callan-Symanzik⁸. This formulation encodes the mathematical apparatus in both quantum field theory and the theories of critical phenomena used to handle problems with singularities.

The statistical mechanics aspects are being now firmly established capitalizing on various investigations inspired openly or implicitly on a Maxwellian approach: several examples presented here have been promoting the transfer from thermodynamics to the field of kinetics introducing procedures for taking “kinetic limits” beyond the usual “thermodynamic limit”.

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Electron-Density Polarization Effects in Molecular Crystals and Bioactive Environments

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Palavras-Chave: *Distributed polarizability, Atom-Dipole Interaction Model, Quantum Theory of Atoms in Molecules.*

Biomaterials are artificial substances incorporated to living systems, or bio-products with applications in materials science and nanotechnology. Despite their good performance, most are developed by trial-and-error instead of being rationally designed. In order to optimize the efficiency of a biomaterial, algorithms enabling accurate selection of candidates according to their functionalities are therefore desirable. In a long-term view, this work aims at developing such methods based on the building blocks of a biomaterial, and on additive approaches to estimate properties of the associated macromolecules.

Whilst any method that enables dividing a large object into small parts is in principle acceptable, a partitioning scheme based on quantum-mechanics is generally preferable. For this reason, algorithms presented here extract building blocks from the electron-density distribution using Quantum Theory of Atoms in Molecules (QTAIM).^[1]

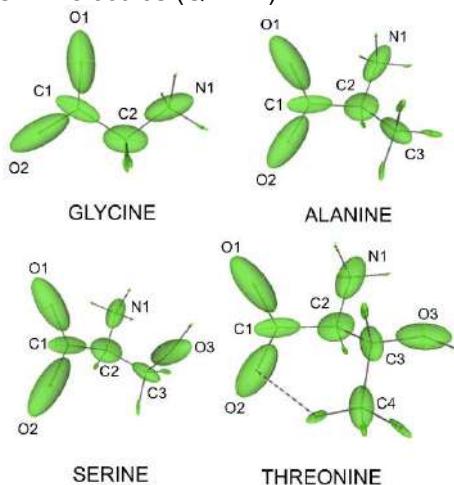


Fig. 1: Distributed polarizabilities of the smallest amino acids, emphasizing the transferability of functional groups.

On the one hand, atomic and functional-group dipole moments, distributed polarizabilities (Fig. 1) and electrostatic potentials (Fig. 2) are quite transferable electro-optical properties among series of molecular or polymeric materials that are at least structurally similar.^[2] One could build a database containing the most prominent atoms or groups for a particular electro-optical behavior, available to materials engineers just to synthesize compounds. On the other hand, because (bio)materials exist in the solid phase (particularly in crystalline forms) or solution, building blocks extracted from very accurate

gas-phase molecular simulations are only representative of the bulk when the chemical environment is properly taken into account. For the case of molecular materials, this necessarily implies account for intermolecular interactions. The best way to estimate condensed phases is through calculations under periodic boundary conditions (either static or dynamic). However, the limited amount of electronic correlation included often hampers accurate predictions. An alternative to account for the environment is to simulate finite molecular aggregates followed by extraction of the electron density of the central molecule, even though results could heavily depend on the size and shape of the chosen clusters. Since intermolecular interactions are usually weaker than intramolecular covalent bonds, semiempirical approaches (based on classical electrostatics) could also be useful to predict electron-density polarization effects due to environment from gas-phase calculations in a kind of local-field perturbation, in which the field experienced by an atom or functional group possesses contributions from all neighboring dipoles (Atom-Dipole Interaction Model – Fig. 2).^[3]

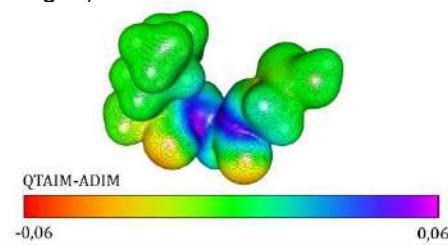


Fig. 2: Electrostatic potential difference for the tripeptide L-leucylglycylglycine in the crystalline phase calculated using QTAIM quantum-mechanical partitioning and ADIM electrostatic approximation.

All these approaches have been developed over the last years by a collaboration involving the Federal University of Minas Gerais, the University of Göttingen and the Polytechnical University of Milan. They are being implemented in the *PolaBer* software whose latest developments will be presented here.

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Advances on Active Learning for Efficient Global Optimization of Atomic Clusters

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Keywords: Machine learning, uncertainty, Bayesian optimization, active learning, automation, DFT and SCC-DFTB.

Abstract

Active Learning (AL) is based on machine learning (ML) and its uncertainty for prediction and decision-making. It has been successfully applied in material science, for instance, for global optimization (GO) of clusters and materials defects [1, 2]. Many important chemistry problems require the structural elucidation of molecules or solids as a first step to the mechanistic elucidation of complex heterogeneous catalysis phenomena.

In this work, we will discuss the progress of the QMLMaterial software [1, 2] for GO of atomic cluster and/or spin multiplicity (SM) by means of AL method. The AL provides an automatic structural elucidation framework where ML algorithms with their uncertainties are used to choose the most promising clusters and/or SM in the non-observed space to be computed [1, 2] from first-principles methods. Thus, increasing the probability of finding the GM. Special attention will be given to the recent advances of our new AL implementation where both structural and SM elucidation are taken inside the loop.

The method was applied for the GO of Na₂₀ and 3Al@Si₁₁ atomic clusters. The local optimization of the structures was done using SCC-DFTB and DFT, respectively. For the 3Al@Si₁₁, the doped configurations and the SMs (2, 4, 6) were considered during the GO. The Gaussian Process (GP) and Neural Network (NN) algorithms were used with the MBTR structural descriptor [3]. For the SM search, a descriptor was developed to include both structural and SM elucidations. The acquisition functions exploitation, exploration and the trade-off (expected improvement) [1] were used for decision making. Genetic algorithm operators were used to sample the non-observed space [4].

Fig. 1 presents the cumulative success as a function of new calculations (local optimizations) obtained for 30 AL independent runs. For the Na₂₀ (left) the AL with NN2, K-fold cross-validation for uncertainty quantification and crossover for sampling presented the best performance. For the 3Al@Si₁₁, where the doped configurations and the SMs were considered in the AL (right), just 50 new calculations were required to achieve a success ~ 80 %.

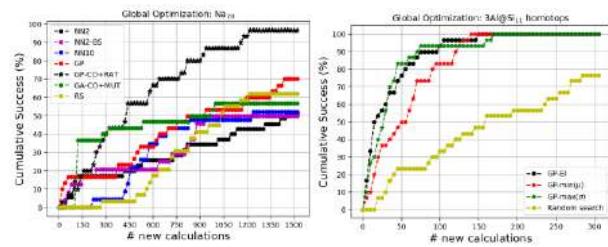


Figure 1. Cumulative success as a function of the number of new calculations. Left: AL for Na₂₀; right: AL for the 3Al@Si₁₁ where different SMs were considered.

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Stability of neutral molecular polynitrogens: Energy content and decomposition mechanisms

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Key-words: Energy-density, Decomposition, Polynitrogens

Introduction

The potential application of all-nitrogen molecules (PolyN) as high energy density materials has been attracting considerable scientific effort. If stable enough to be synthesized and stored, these systems may be used as a green source of energy, since, the only product of their decomposition would be molecular nitrogen, which possesses one of the strongest known covalent bond. However, it is very difficult to obtain these structures under mild experimental conditions. One of the main factors that can help this sort of analysis is the prediction of the activation energy barriers of these structures towards unimolecular decomposition^[1,2].

In this work, we explore the stability and decomposition of several neutral molecular PolyN of different sizes and shapes using a common and accurate theoretical methodology in order to compare among them, search for patterns and identify potential candidates for synthesis.

Methodology

The calculation method was based on density functional theory (DFT), using exchange and correlation functionals that are known for their high accuracy in predicting barriers heights^[3] (M06-2X and SOGGA11-X). An extensive search for transition states (TSs) that connected the initial structures to unimolecular decomposition was performed. After finding the TSs, an intrinsic reaction coordinate calculation was carried out for each polyN in order to confirm the decomposition mechanism found.

For this initial and exploratory part of the work, the SOGGA11-X/def2-SVP level of theory was used. A refinement of the results was then performed at the M06-2X,SOGGA11-X/def2-TZVPP levels, being the energies zero pointed corrected. The activation energies (AEs) and the dissociation energies (DEs) of each polyN were calculated at the refined level as:

$$AE = E_{TS} + ZPE_{TS} - [E_{PolyN} + ZPE_{PolyN}]$$

$$DE = E_{PolyN} + ZPE_{PolyN} - \frac{n}{2}[E_{N_2} + ZPE_{N_2}]$$

where n is the total number of atoms of the PolyN.

For a structural and electronic analysis of the systems, the average bond lengths, average bond orders, HOMO-LUMO gaps and asphericities were calculated.

Results

The results indicate (Fig. 1)^[4] that the prismatic caged polyN can be expected to present higher energy densities (higher DE) and be more stable with respect to unimolecular decomposition (larger AE), being the $N_8(C_{2v})$ -B structure a surprising exception.

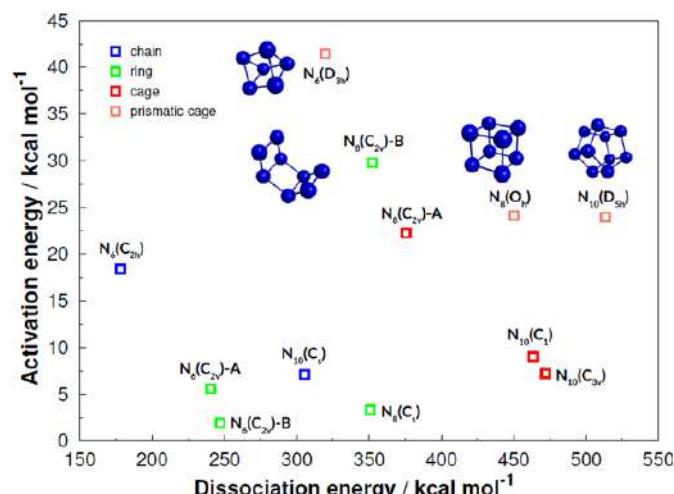


Fig. 1: Evans-Polanyi plot for all polyN structures.

Conclusions

After the completion of this work, it was possible to achieve a correlation between the systems and their energy content. However, it was not possible to assess a clear correlation between the activation energy barriers with the calculated structural and electronic properties.

Acknowledgements



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XXI SBQT

Descoberta de um Inibidor Nanomolar da Mieloperoxidase Oralmente Ativo em um Modelo de Artrite Gotosa usando uma Regra Inibidor-símile e Triagem Virtual Baseada no Receptor.

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Palavras-Chave: *Triagem virtual, inibidor, mieloperoxidase, artrite gotosa.*

Introdução. Os neutrófilos são as células responsáveis pela resposta inicial contra patógenos^{1,2}, sendo a enzima mieloperoxidase (MPO) a responsável pela produção de HOCl, um importante oxidante que pode causar danos aos tecidos³. Estudos indicam que a MPO é um importante mediador da inflamação e do dano nas articulações⁴. Recentemente, o binômio Neutrófilo/MPO tem sido implicado na patogênese da insuficiência respiratória aguda grave na doença pandêmica Covid-19⁵. Neste contexto, a MPO surge como um promissor alvo molecular.

Metodologia. O perfil inibidor-símile foi desenvolvido pela análise de propriedades moleculares de inibidores descritos previamente. Para as simulações de docagem molecular, foram usadas três estruturas cristalográficas (PDB 1CXP, 4C1M e 5WDJ). Aminoácidos flexíveis foram identificados através da superposição de 13 estruturas cristalográficas. Foram realizadas correções nos estados de protonação de resíduos. Para otimizar as simulações de docagem, a carga do átomo de ferro hêmico foi calculada usando diferentes Hamiltonianos semi-empíricos. As docagens foram testadas usando os programas AutoDock 4.2.3, AutoDock Vina 1.1.2, e GOLD 5.4. A capacidade discriminatória de cada programa foi avaliada por meio de métricas estatísticas. As docagens moleculares foram validadas por “redocagem” e docagem cruzada. Os “hits” computacionais foram validados por ensaios enzimáticos e celulares. Os estudos *in vivo* foram conduzidos em um modelo murino de artrite gotosa induzida por cristais de ácido úrico.

Resultados. A análise das propriedades moleculares de inibidores conhecidos indicou que compostos que satisfazem as propriedades de massa molecular (176 - 396 u.m.a.), logP (0,1 - 4,37), nDH (0 – 7), nAH (2 – 9), nROT (0 – 8) e TPSA (18 - 122) possuem alta probabilidade de inibir da MPO. A sobreposição de diferentes estruturas cristalográficas da MPO indicou a presença de 3 resíduos flexíveis (Glu116, Asp218, Met411), embora localizados externamente ao sítio ativo. O cálculo da carga do átomo de ferro hêmico indicou que o Hamiltoniano PM7 reproduz melhores conformações

experimentais de ligantes co-cristalizados. Métricas estatísticas robustas indicaram que as funções ASP e CHEMPLP, presentes no programa GOLD, possuem desempenho superior na discriminação entre inibidores e não inibidores. A aplicação das regras inibidor-símile ao banco de dados ZINC 12, recuperou 6546 compostos que satisfazem os critérios. A docagem desse conjunto pelo programa GOLD recuperou 242 moléculas que tiveram seus modos de ligação confirmados pelo AutoDock, resultando em 28 hits computacionais. Testes enzimáticos confirmaram atividade inibitória de 18 compostos, sendo o inibidor ILR6 o composto de maior atividade ($IC_{50} = 0,28 \pm 0,07 \mu M$), inibindo a atividade clorinante celular e o edema de pata induzido por cristais de ácido úrico quando administrado tanto por via intraperitoneal quanto por via oral.

Conclusões. O uso de uma metodologia computacional validada, que integra uma regra inibidor-símile e triagem virtual baseada no receptor demonstrou-se eficaz na descoberta de inibidores da MPO ativos por via oral em um modelo de artrite gotosa. O inibidor obtido a partir deste estudo tem potencial aplicação na terapêutica anti-inflamatória.

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Computational design of synthetic receptors for drug detection: interaction between molecularly imprinted polymers and MDMA (3,4-methylenedioxymethamphetamine)

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Palavras-Chave: *theoretical calculations, rational design, artificial receptors.*

Introduction

For many decades, synthetic receptors have been used as sensor elements and are a promising alternative to natural receptors, which, despite its great selectivity, are so complex and unstable¹. The rational design of this kind of receptors is currently one of the most researched topics in molecular recognition². Molecular imprinted polymers (MIPs) have become a growing highlight in polymer chemistry, once they possess a wide range of applications and can be used in several environments, due to their high chemical and thermal stability³. The aim of this study was to perform a rational design for the MIP preparation, for 3,4-methylenedioxymethamphetamine (MDMA) detection.

Methodology

The theoretical calculations were employed at several stages of the process, using DFT and B3LYP/6-31G(d,p) level of theory, by means of optimization and frequency calculations.

Results

Among the several functional monomers tested, the itaconic acid (IA) was the most appropriated for MIP preparation with MDMA template, and the proper molar ratio found theoretically was 3:1 (IA:MDMA), as showed in Table 1.

Table 1 Interaction energy variation (ΔE) values for each monomer-template complex at 1:1, 1:2 and 1:3 molar ratios.

Molar Ratio	ΔE (kcal.mol ⁻¹)		
	1:1	1:2	1:3
Acrylic acid (Al)	-176.58	-196.14	-220.82
Itaconic acid (Al)	-192.42	-231.03	-285.01
Metacrylic acid (MA)	-174.79	-192.43	-215.65
Acrylamide (ACL)	-180.33	-201.61	-238.57
Acrolein (ACRO)	-165.91	-176.34	-186.78
Divinylbenzene (DVB)	-167.58	-179.16	-189.13
Styrene (ST)	-163.16	-168.93	-176.13
Methyl methacrylate (MMA)	-171.38	-184.59	-197.30
Trifluoro methacrylate (TFMA)	-173.97	-194.80	-217.45
Vinylimidazole (VI)	-160.58	-161.03	-173.60
Vinylpiridine (VP)	-163.35	-166.33	-175.85

In the preparation of pre-polymerization complex, polar solvents were found to perform a better stabilization, mainly those which are not protic solvents. As cross-linking agents, the better results were obtained for trimethylolpropane trimethacrylate (TRIM) and ethylene glycol dimethacrylate (EGDMA) molecules, respectively. Finally, selectivity tests showed a high affinity of the studied MIP for MDMA and chemically similar molecules (Table 2).

Table 2: Interaction energy (ΔE) and relative interaction energy values (ΔE_{rel}) (kcal.mol⁻¹) for templates in the selectivity test.

Template	ΔE (kcal.mol ⁻¹)	ΔE_{rel} (kcal.mol ⁻¹)
AP	-113.64	15.29
MA	-114.13	14.80
MC	-119.34	9.59
MDA	-128.80	0.12
MDEA	-127.98	0.95
MDMC	-124.41	4.51
MDMA	-128.93	0.00
ALEPH	-108.84	20.08
2CB	-117.41	11.52
2CD	-118.54	10.39
DMT	-104.97	23.96
MEM	-105.48	23.45

Conclusion

The proposal theoretical strategy yielded novel, experimentally testable hypotheses for the design of MIPs. Additionally, from the theoretical point of view, the set of computational analyses presented in this paper constitutes a very useful protocol to predict optimal experimental conditions, which can considerably reduce the time and cost on the MIPs preparation.

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Mott-Anderson Metal-Insulator Transitions from Entanglement in Disordered Nanostructures

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Keywords: quantum phase transitions, entanglement, density functional theory

A metal can be driven to an insulating phase through distinct mechanisms. A possible way is via the Coulomb interaction, which then defines the Mott metal-insulator transition (MIT). Another possibility is the MIT driven by disorder, the so-called Anderson MIT. Here we analyze interacting particles in disordered Hubbard chains – thus comprising the Mott-Anderson physics – by investigating the ground-state entanglement with density functional theory [1].

The localization signature on entanglement is found to be a local minimum at a certain critical density. Individually, the Mott MIT (Figure 1) and the Anderson MIT (Figure 2), have a single critical density whose minimum entanglement decreases as the interaction (disorder) enhances. While in the Mott MIT entanglement saturates at finite values, characterizing partial localization, in the Anderson MIT the system reaches full localization, with zero entanglement, for sufficiently strong disorder.

In the combined Mott-Anderson MIT (Figure 3), we find three critical densities referring to local minima on entanglement. One of them is the same as for the Anderson MIT, but now the presence of interaction requires a stronger disorder potential to induce localization. A second critical density is related to the Mott MIT, but due to disorder it is displaced by a factor proportional to the concentration of impurities. The third local minimum on entanglement is unique to the concomitant presence of disorder and interaction, found to be related to an effective density phenomenon, thus referred to as a Mott-like MIT.

Since entanglement has been intrinsically connected to the magnetic susceptibility – a quantity promptly available in cold atoms experiments – our detailed numerical description might be useful for the experimental investigation of Mott-Anderson MIT.

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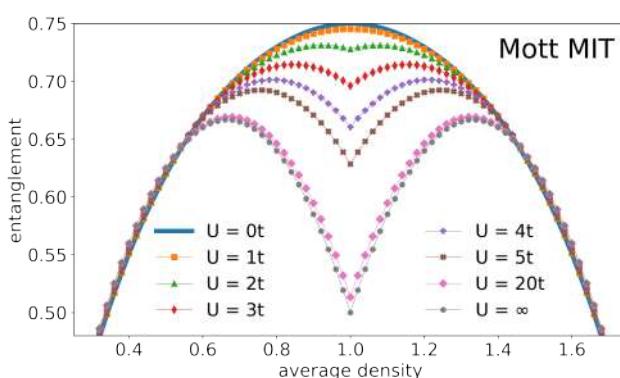


Fig. 1: Mott Metal-Insulator transition for $V = 0$.

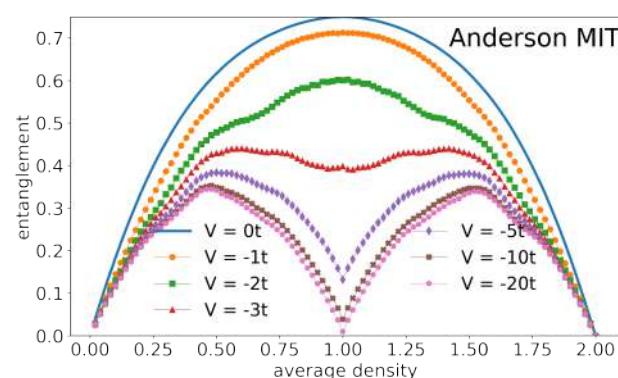


Fig. 2: Anderson Metal-Insulator transition for $U = 0$.

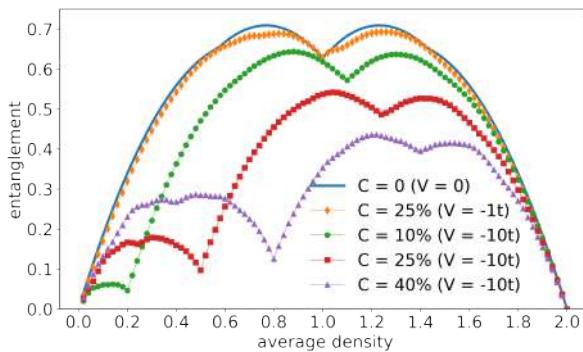


Fig. 3: Mott-Anderson Metal-Insulator transition for $V \neq 0$ and $U \neq 0$.

Unraveling the Complex Mechanism of an Asymmetric Catalysis: the Michael-Type Addition of Nitromethane to Enone Catalyzed by a Bifunctional Primary Amino-Thiourea

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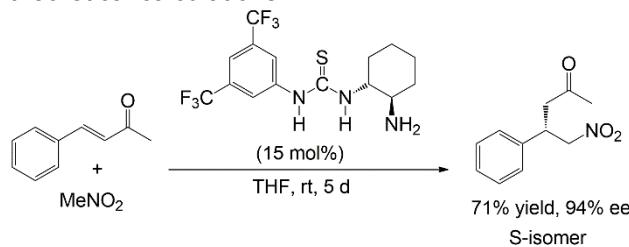
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Key-Words: *Iminium mechanism, additive effect, DFT.*

Introduction

Bifunctional primary amino-thiourea (APTB) is an asymmetric catalyst used some years ago in the Michael-type addition (Scheme 1) of nitromethane to enone, leading to good yields and high ee.^[1] Although a base-catalyzed mechanism was suggested by the authors, the primary-amine group could also work via an iminium ion catalysis. The objective of this work is to investigate both of the mechanisms via reliable theoretical calculations.



Scheme 1. Michael-type addition catalyzed by APTB investigated in this work.

Methodology

Geometry optimizations and vibrational frequency were performed at X3LYP/def2-SVP (ma-def2-SVP for oxygen and nitrogen atoms) level of theory. Single point energy calculations were done at M06-2X/def2-TZVPP (ma-def2-TZVPP for oxygen and nitrogen atoms) level of theory for obtain more reliable values of electronic energy. The solvent effect was included via single points calculations at SMD/X3LYP/def2-SVP (ma-def2-SVP for oxygen and nitrogen atoms) level of theory, using tetrahydrofuran (THF) as the solvent.

Results

Initially, we investigated the viability of a base-catalyzed mechanism from the transition states of carbon-carbon bond formation and although different configurations were considered, they all presented activation ΔG^\ddagger barriers above 37.0 kcal mol⁻¹, which makes this pathway kinetically unfeasible. An iminium ion mechanism was also investigated. This mechanism is very complex with many steps, and the first one is the formation of carbinolamine from the reaction between APTB and enone. In this step, we have found that the formation of this intermediate needs a cocatalyst, which was modeled as being acetic acid. Depending on the solvent, carboxylic acids can be present as a contaminant. In

addition, in many reactions of this type, carboxylic acids are used as additive. In the next step, the formation of an imine from dehydration of carbinolamine, is also acid-catalyzed. The formed imine intermediate can deprotonate nitromethane, leading the formation of the nitronate-iminium ion-pair. This is the rate-determining step and the predicted kinetics is compatible with experimental data. The following step is the formation of carbon-carbon bond, which is the enantioselective step. The S enantiomer is predicted to be the main product, in agreement with experimental observations. The next steps are the formation of a second imine, a second carbinolamine and finally, the formation of the product and the catalyst recovery. Again, acetic acid works as a cocatalyst.^[2]

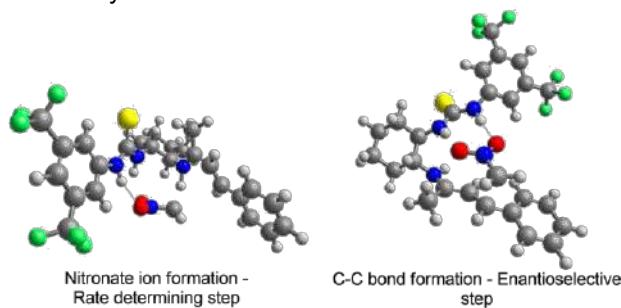


Figure 1. Transition state structures involved in important steps in the imine mechanism.

Conclusions

The theoretical study conducted in this work has at the first time elucidated the reaction mechanism of the APTB catalyzed Michael-type addition of nitromethane to enone. In addition, we have showed the important role of an acid in the mechanism, which works as a cocatalyst in several steps. This study is an important contribution for elucidating this kind of catalysis and can be useful for more catalyst design.

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Maintenance of the secondary structure of mellitin in water and in the ionic liquid [BMI][OAc]

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Keywords: *Ionic liquids, polypeptide, secondary structure*

Introduction – Ionic liquids (ILs) are molten salts with fusion temperatures below 100 °C. Such substances have been studied for a long time for their use in fields such as catalysis, biocatalysis and pharmacy.¹ The solvation of proteins by neat ILs is important for the biocatalysis in non-aqueous media² and for the preservation of proteins under high temperatures and during long periods.³

Mellitin (figure 1) is a toxic peptide, soluble in water, present in bee venom (*Apis mellifera*). It presents a helical structure and is composed of 26 aminoacids, bearing a +5 net charge, +4 of which are in its C-terminal portion.⁴

In the present study, we aimed at analyzing, through Molecular Dynamics (MD) simulations, the structural differences of the polypeptide mellitin when dissolved in water and when dissolved in the 1-butyl-3-methylimidazolium acetate IL (whose structure is depicted in figure 2).



Figure 1 – Mellitin, in the ribbon representation.

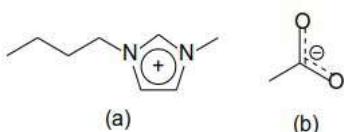


Figure 2 – Ions of the [BMI][OAc] IL: 1-butyl-3-methylimidazolium cation (a) and the acetate anion (b).

Metodology – The GROMACS⁵ software package (version 4.5.5) was used in this work for performing the MD simulations and analysis. The systems were simulated in the isothermal-isobaric (NpT) ensemble, with temperature kept at 298.15 K and pressure kept at 1.0 bar. The system corresponding to one mellitin molecule solvated in water consisted of the polipeptide, 10290 water molecules and 5 chloride ions. For the polipeptide in the neat IL, 1113 [BMI] cations and 1118 [OAc] anions were used.

Results and discussion – For the analysis of the structural differences of mellitin in water and in the neat IL, the root mean square displacement

(RMSD), radius of gyration and secondary structure of the polipeptide were considered (figure 3). The RMSD indicates a greater mobility of mellitin in water; the IL seems to preserve to a greater extent the initial structural arrangement of the polipeptide. In a similar way, the radius of gyration is more constant in the case of the IL, whereas the decrease of this parameter in the aqueous system suggests the collapse of mellitin. Finally, the analysis of the secondary structure shows that, in water, during the course of the simulation, there is a greater variation in the number of residues participating in alpha-helices.

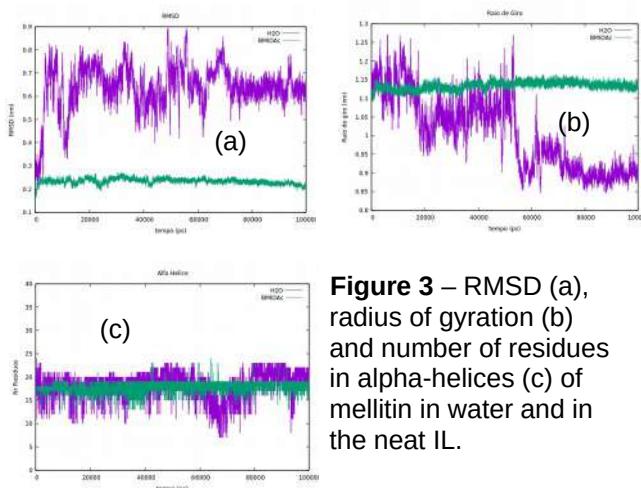


Figure 3 – RMSD (a), radius of gyration (b) and number of residues in alpha-helices (c) of mellitin in water and in the neat II

Conclusion – The information gathered in this study suggests that the [BMI][OAc] IL presents a greater efficacy in maintaining the secondary structure of mellitin, when compared to water.

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In silico analysis of human SOD1 protein variants related to Amyotrophic Lateral Sclerosis

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Keywords: Amyotrophic Lateral Sclerosis, Superoxide Dismutase 1, In Silico.

INTRODUCTION: Amyotrophic lateral sclerosis (ALS) is the most frequent motor neurodegenerative disorder in adults. Missense mutations in superoxide dismutase 1 (SOD1), a major cytoplasmic antioxidant enzyme, are associated with the development of ALS. The A4V and D90A variants account for approximately half of all ALS-SOD1 cases in the United States and Europe. This work aims to characterize *in silico* the structural and functional effects of A4V and D90A variants on human SOD1 protein.

Understanding the effects of SOD1 mutations on protein structure facilitates the design of further experiments and provides relevant information on the molecular mechanism of pathology, which may contribute to improvements in existing treatments for ALS.

METHODOLOGY: Three-dimensional structures of A4V and D90A protein variants were computationally modeled in the VMD-1.9.1 package using the experimentally determined structure of wild-type SOD1 (PDB ID: 2C9V) as the template. Molecular dynamics (MD) simulations of the wild-type SOD1 protein and its variants A4V and D90A were performed in triplicates using the GROMACS-2018.8 package and AMBER99SB-ILDN force-field. TIP3P water molecules were added to a dodecahedral box system, which was neutralized by the addition of Na⁺ Cl⁻ ions and then minimized. The system also had its temperature and pressure equilibrated at 1atm and 300K before the start of the simulations, which lasted 300ns. The MD trajectories were concatenated, and the following parameters were analyzed using GROMACS distribution programs: root-mean-square deviation, root-mean-square fluctuation, B-factor, radius of gyration (Rg), solvent accessible surface area (SASA), secondary structure, and essential dynamics. **RESULTS:** The triplicates for wild-type SOD1 and its variants presented a similar behavior throughout the simulation. The establishment of a plateau in RMSD, Rg, and SASA values after approximately 150ns indicates that the protein structures fluctuate around average stable conformations and, consequently, system equilibration. The MD analyses of variants A4V and D90A pointed to flexibility and essential dynamics alterations at the electrostatic and metal-binding loops, which are functional domains

indispensable for SOD1 enzymatic activity, substrate guidance, and structural stability. Considering that structural flexibility and dynamics are key factors that drive protein interactions, our findings indicate that A4V and D90A may affect SOD1 interactions, particularly at the functional loops. A well-accepted hypothesis suggests that dynamics and structural alterations at the electrostatic and metal-binding loops of SOD1 could lead to ALS possibly through a toxic mechanism involving aberrant protein interactions triggering aggregation.

CONCLUSIONS: Our findings pointed to alterations at the A4V and D90A variants that may have harmful implications for SOD1 and possibly explain their association with the development of ALS.

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Modeling of the Water/Pd(111) Interface using a QM based polarizable force field

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Palavras-Chave: *Polarizable force fields, Molecular dynamics, Water/Metal interface*

Aqueous electrochemical interfaces are of extreme importance for several technological applications. Therefore, the microscopic understanding and control of such interfaces play a key role in the development of fuel cells, batteries, photovoltaic systems, among other technologies.

Besides that, the water plays a key role as solvent or reagent in several electrochemical processes, such as electrolysis, corrosion, and electro catalysis. Thus, the microscopic understanding of the kinetic behavior and reactions that occur in water/metal interface is essential.

In this manner, atomistic simulations have shown to be a versatile tool to assist experimental studies providing a detailed comprehension and description of such interfaces at the atomic and molecular level. Concerning the quantum aspects and the size of such systems, multiscale simulations based on hybrid QM/MM (Quantum Mechanics/Molecular Mechanics) methods seems to be an efficient approach to describe the physical and chemical process at the electrode interface since the combination of ab-initio and empirical methods allows the dynamical study of systems with large sizes and time scales without neglecting the reactivity of the metallic surface.

One of the key elements in QM/MM approaches is the classical force field. Particularly for metals, the accuracy of the simulation strongly relies in the ability of the force field to reproduce surface polarization effects. Based on this, we develop suitable polarizable force fields to describe the water/metal interface. Charged virtual sites are added to the molecular topology of a simple LJ model in order to create dipoles that reproduce the surface polarization. In this way, the metallic system is composed of permanent dipoles created by rods (so-called Rod model).

The development of the polarizable force field for the water/Pd(111) interface based on the Rod model is done by following a systematic computational protocol that involves QM, QM/MM and MM calculations, which can be summarized as follows:

- A. Geometry optimization of selected structures using QM;
- B. Determination of the induced electrostatic potential using QM/MM;
- C. Charge fitting;
- D. Fitting of non-bonded Lennard-Jones parameters for the Oxygen-Metal and Hydrogen-Metal pairs.

The proposed model was tested and adjusted in order to reproduce the polarization and adsorption properties of the water/Pd(111) systems, being our results in a good agreement with the QM results and experimental information available in the literature for the Pd(111)/water systems at fixed temperature.

Funding Acknowledgment

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Reação de Friedel-Crafts: Estudo Teórico do Mecanismo de Alquilação de Benzeno com Cloreto de Alquila promovido por AlCl_3

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Palavras-Chave: Mecanismo de reação, Alquilação, Ácido de Lewis

Introdução: Uma etapa relevante na síntese orgânica é a formação de ligações carbono-carbono.^{1,2} A reação de Friedel-Crafts tem uma aplicação importante neste sentido, principalmente para a alquilação e acilação de compostos aromáticos.^{1,2} No caso da alquilação, a metodologia consiste na utilização de um ácido de Lewis, mais comumente o AlCl_3 , com a finalidade de ativar o haleto de alquila para promover o ataque eletrofílico ao composto aromático.^{1,3} Alguns estudos teóricos e experimentais têm explorado as interações entre o catalisador e os reagentes da reação de Friedel-Crafts.⁴ No entanto, até o momento ainda não é muito claro o mecanismo exato destas reações, nem o perfil de energia livre da reação é disponível. Assim, neste trabalho estudamos as reações de alquilação do benzeno (BZ) com cloreto de etila (EtCl) e n-propila ($n\text{-PropCl}$) nos solventes acetonitrila (CH_3CN) e benzeno. Os objetivos principais foram: obter as geometrias dos estados estacionários referentes aos complexos do catalisador com os reagentes e os respectivos estados de transição (TS) da reação. Esperamos que seja possível obter o mecanismo da reação compatível com a cinética experimental. As geometrias foram obtidas utilizando a teoria do funcional de densidade (DFT) com o funcional X3LYP e funções de base do tipo def2-SVP.⁵ A energia eletrônica foi obtida utilizando o funcional M06-2X com funções de base def2-TZVPP.⁶ As propriedades termodinâmicas em fase gasosa foram determinadas via cálculos de frequências harmônicas, utilizando a mesma metodologia usada para obter as geometrias. A energia livre de solvatação foi obtida utilizando o modelo SMD com o funcional X3LYP e as funções de base 6-31(+G(d)).⁷ Para os cálculos foram utilizados os programas GAMESS e ORCA.^{8,9}

Resultados e discussão: Primeiramente foi avaliada a possibilidade de formação de complexos maiores de AlCl_3 . Em benzeno o ΔG de formação do dímero (Dim), trímero, tetrâmero, e pentâmero são iguais a -16,77, -20,60, -26,14 e -29,88 kcal/mol respectivamente. De fato, nos dois solventes, a estabilização por unidade monomérica é maior no Dim, sendo, por exemplo, 1,51 kcal/mol mais estável que no caso do trímero no solvente benzeno. Já o valor do ΔG referente a complexação do AlCl_3 com benzeno é igual a -4,15 e -3,60 kcal/mol nos solventes BZ e CH_3CN , respectivamente, indicando que esse processo é menos favorável que a dimerização do AlCl_3 . A complexação do AlCl_3 com EtCl apresenta valores de ΔG iguais a -7,22 e -7,42

kcal/mol em BZ e CH_3CN , respectivamente. No solvente CH_3CN este complexo é mais estável que o Dim. Assim, o ΔG^\ddagger da reação foi calculado em relação ao complexo em CH_3CN e em relação ao Dim, EtCl e BZ separados em BZ. Os valores calculados de ΔG^\ddagger da primeira etapa (TS apresentado na figura 1) são iguais a 27,94 e 25,54 kcal/mol em BZ e CH_3CN respectivamente. No caso do 1-PropCl e do 2-PropCl, os valores de ΔG da complexação com o AlCl_3 são iguais a -6,60 e -6,84 kcal/mol em BZ e CH_3CN , respectivamente. Como esses valores são maiores que o ΔG de dimerização por unidade monomérica de AlCl_3 , o Dim e os demais reagentes separados foram tomados como referência para o cálculo das respectivas barreiras. O ΔG^\ddagger da primeira etapa da reação entre o 1-PropCl e BZ é igual a 27,43 e 24,05 kcal/mol em BZ e CH_3CN , respectivamente, enquanto que, no caso da reação com 2-PropCl, os valores são iguais a 21,80 e 16,49 kcal/mol. As etapas seguintes são rápidas e envolvem a transferência de próton, a respectiva formação do produto alquilado e a regeneração do catalisador.

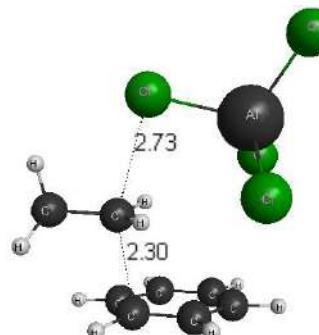


Figura 1. Geometria do TS da alquilação com EtCl .

Conclusões: O catalisador apresenta-se na forma de dímeros. A formação de complexos de AlCl_3 com EtCl é favorável apenas em CH_3CN , o que não ocorre com $n\text{-PropCl}$. Pretendemos ainda avaliar a participação de carbocátions e o papel do AlCl_3 na isomerização do $n\text{-PropCl}$.

Agradecimentos: CAPES, CNPq, FAPEMIG

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Passivação de Perovskitas de iodeto de Metilamônio e Chumbo com moléculas orgânicas: o caso da molécula 4-terc-butil piridina (TBP)

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Palavras-Chave: MAPbI₃, DFT-SIESTA, TBP.

INTRODUÇÃO

Por suas excelentes propriedades estruturais e eletrônicas, a perovskita de iodeto de metilamônio e chumbo (MAPbI₃) tem sido uma das mais estudadas na produção de células solares, que até agora tem atingido uma eficiência de conversão de energia (PCE) de 25.5 % segundo o NREL. Apesar disso, os problemas de estabilidade da estrutura do material ainda precisam ser resolvidos. A fase ortorrômbica deste material tem sido escolhida para estudos teóricos deste tipo¹, com a escolha da passivação de superfícies/interfaces da perovskita como uma das estratégias de maior sucesso. Diversas moléculas, que vão desde ácido/bases de Lewis até halogenetos de amônio quaternário (QAHs)², são testadas na passivação de defeitos iônicos carregados o que leva por sua vez para uma melhoria na PCE e outras propriedades optoeletrônicas. As moléculas de base de Lewis que modificam a estrutura da perovskita são particularmente eficazes para a passivação. Experimentalmente 4-terc-butil piridina (TBP) tem sido introduzida no anti-solvente da MAPbI₃ para obter camadas de perovskita de alta qualidade e estabilidade³. O TBP utilizado com aditivo multifuncional desempenha um papel positivo no aumento da fotovoltação dos materiais^{4, 5}. Assim, neste trabalho foi estudado o efeito da adsorção do TBP puro e com adição de íons de Cl⁻, I⁻ ou Br⁻ na superfície de perovskitas ortorrômbicas de MAPbI₃.

MÉTODOS

Empregamos cálculos de primeiros princípios baseados na DFT⁶ como implementado no método SIESTA⁷ com uso de pseudopotenciais de norma conservada na forma fatorada de Kleinman-Bylander⁸. Usamos para a aproximação do funcional de troca e correlação o GGA/PBE⁹ e vdW-BH¹⁰. Para as integrais no espaço real utilizamos um grid definido por um meshcutoff de 350Ry. As geometrias foram considerados otimizadas quando a máxima força em qualquer átomo era menor do que 10meV/Ang. Após da otimização e caracterização do bulk da MAPbI₃ ele foi replicado na direção dos índices de Miller (010) para obter slabs com superfície terminada em iodeto de chumbo (PbI₂). Inicialmente foram testados slabs 2x1 (2 camadas de PbI₂ e 1 camada de iodeto de metilamônio (MAI)), sobre os quais foram adsorvidas uma molécula de TBP pura e com a adição de íons de Cl⁻, I⁻, Br⁻.

RESULTADOS

Propriedades estruturais como o parâmetro de rede do bulk da perovskita ou a energia de superfície apresentam resultados mais próximos dos reportados experimentalmente e teoricamente na literatura, quando usado o funcional vdW-BH. Embora o desvio desses resultados possam ser melhorados ao usar pseudopotenciais mais apropriados em função dos tipos de átomos a serem modelados. A adsorção da molécula de TBP na superfície do slab 2x1, é produzida pela ligação entre a molécula de N do TBP e o átomo de Pb da superfície do slab. O gap do sistema é apenas 0.03 eV menor do que o sistema sem TBP. A energia de adsorção da TBP ao slab é de -0.58 eV. A adsorção da molécula no slab leva à uma alteração nos picos da PDOS em relação ao slab puro. Isso pode ser um indicativo de prováveis alterações em traps states das supercícies da perovskita. A presença dos íons Cl⁻, I⁻ ou Br⁻ no slab 2x1 passivado com TBP induzem estados localizados na sua superfície, o que por sua vez induz um comportamento magnético do slab, que é evidenciado pela ligeira assimetria da PDOS para o caso dos átomos de Iodo do slab e os íons adsorvidos.

CONCLUSÕES E PERSPECTIVAS

O gap de energia não é significativamente alterado pela presença da molécula de TBP na superfície de um slab 2x1 de MAPbI₃. Após da adsorção da molécula de TPB no slab, momentos magnéticos podem ser induzidos pela presença de íon de Cl⁻, I⁻ ou Br⁻ na superfície do slab. O efeito da espessuras do slab (3x2, 4x3 e 5x4) será pesquisado seguido a mesma metodologia.

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UFOP-PROPPI, FAPEMIG, OEA/GCU, CNPq, CAPES

Adsorption of arsenic compounds on subunits of Metal-Organic Frameworks – an *in silico* approach to water treatment

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Keywords: Density Functional Theory, Materials design, MOFs

Introduction

The removal of arsenic compounds from water bodies is considered a priority issue for developing technologies by the World Health Organization (WHO) [1]. These substances have acute toxicity and are carcinogenic [2], with an estimate that more than 70 countries possessed contaminated waters, so that around 140 million people are affected [3].

The arsenic compounds can be removed from aqueous systems using adsorbents. An interesting class of materials to be used in this application are the Metal-Organic Frameworks (MOFs), because of the possibility of preparing them with properties adjusted to the application purposes. The MOFs are porous crystalline solids obtained by combining two subunits, which are metallic agglomerates and divergent organic ligands [4]. In this work, computer simulations based on Density Functional Theory (DFT) were performed to investigate the characteristics of the subunits that could favour the adsorption of arsenic compounds on MOFs.

Methodology

The DFT simulations were performed using the program ORCA 4.2.1 at PBE-D3BJ/def2-TZVP level of theory. The subunits of MOFs evaluated (Figure 1) were the ligands H₂BDC and H₃BTC, besides the metallic agglomerates of zinc paddlewheel (pdw) and aluminium trigonal prism (pt).

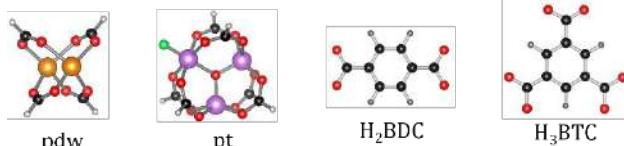


Figure 1. Investigated subunits of MOFs. Legends of atoms: Zn (orange), Al (violet), C (black), H (grey), O (red), and F (green).

The adsorptions of the following arsenic species were investigated: AsH₃, HAsO₂, H₃AsO₃, HAsO₃, H₃AsO₄ and H₂CH₃AsO₃. The adsorptions of water, as well as other species frequently found in aqueous systems, such as Cl⁻, HSO₄⁻ and H₂PO₄⁻, were also examined to identify possibilities of interference in the adsorption of arsenic contaminants.

Results and discussions

The adsorption energies were estimated (Table 1) being observed that the adsorption process takes place preferably on pdw and pt than on H₂BDC and H₃BTC subunits. The comparison between the analysed metallic agglomerates indicated that the adsorption processes of arsenic species, and also of the interferents, are more favourable on pdw than on

pt. The competition of the water molecules by the adsorptive sites shows to be relevant in the remotion of AsH₃ and H₃AsO₃ from contaminated water. Furthermore, the other species Cl⁻, HSO₄⁻ and H₂PO₄⁻ were identified as important interferences to the adsorption of all analysed arsenic compounds.

Table 1. The Gibbs free energy variation (ΔG) is given in kcal mol⁻¹ at 298 K for the adsorption processes of arsenic and interfering species in the subunits of MOFs.

Species	ΔG			
	pdw	pt	H ₂ BDC	H ₃ BTC
H ₂ CH ₃ AsO ₃	-21.74	-15.87	5.33	1.83
AsH ₃	-1.48	2.15	6.50	6.34
H ₃ AsO ₃ (a)	2.20	5.16	6.26	4.96
H ₃ AsO ₃ (b)	-10.24	-7.38	*	*
H ₃ AsO ₄	-20.21	-14.54	-0.51	2.10
HAsO ₂ (a)	-28.77	-17.92	-9.90	-8.42
HAsO ₂ (b)	-10.03	-8.03	*	*
HAsO ₃	-22.28	-16.96	0.88	5.58
H ₂ O	-5.87	-7.74	5.04	5.71
Cl ⁻	-59.80	-56.69	-19.77	-23.57
HSO ₄ ⁻	-41.28	-32.43	1.34	-0.29
H ₂ PO ₄ ⁻	-38.42	-43.97	0.53	-0.85

(a) and (b) correspond to the coordination by the arsenic and oxygen atoms on the metallic site of the subunit, respectively. The adsorption only occurs by the oxygen atom for the other arsenic compounds.

* There is no data.

Conclusions

The *in silico* study unveiling the preference of the arsenic compounds by the metallic agglomerates when compared to the ligands. Moreover, the pdw might show better performance than pt subunit to the remotion of arsenic compounds from water. As a perspective, it is relevant to investigate the metallic subunits constituted by other metals to verify if they can improve the adsorption process of the contaminants. The dissociated species originated from the analysed arsenic compounds should also be investigated for a more reliable study considering aqueous systems.

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Molecular modelling of the emerging contaminants adsorption on subunits of MOFs aiming the adsorbents design

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Keywords: Density Functional Theory, Materials design, MOFs

Introduction

Emerging contaminants are substances that were not frequently monitored in water, soil, and air, such as analgesics, antibiotics, pesticides, hormones, personal care products and stimulants, but which can have negative impacts on the environment, as the feminization of fishes [1]. These substances reach water bodies through residential effluents, industrial or agricultural activities. However, conventional methods of treating water and sewage are not able to remove them from aqueous systems [2].

Absorption methods for removing these contaminants from water are interesting options due to their simplicity and low cost. An attractive class of porous crystalline materials to be used in this kind of methods are the Metal-Organic Frameworks (MOFs), once it is possible to prepare them with optimized properties to the desired application [3]. The MOFs are constituted by two subunits: organic ligands and metallic agglomerates [4]. Molecular modelling studies based on Density Functional Theory (DFT) were performed in this work aiming to identify important aspects to be considered in the design of MOFs as adsorbents to the remotion of emerging contaminants from waters.

Methodology

The computational simulations were performed at PBE-D3BJ/def2-TZVP level of theory using the program ORCA 4.2.1. The studied emerging contaminants were caffeine (stimulant), triclosan (bacteriostatic agent) and atrazine (pesticide). The analysed subunits of MOFs were the metallic agglomerates of zinc paddlewheel (pdw) and aluminium trigonal prism (pt), besides the ligands H₂BDC and H₃BTC (Figure 1). Some species frequently found in aqueous systems, such as Cl⁻, HSO₄⁻ and H₂PO₄⁻, were examined to obtain information about the possibility of interference in the adsorption processes.

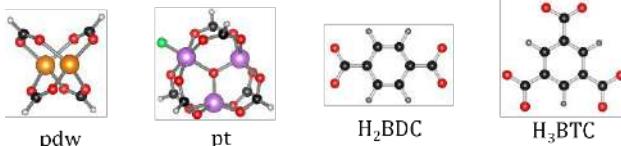


Figure 1. Subunits of MOFs examined to the adsorption of emerging contaminants. Legends of atoms: Zn (orange), Al (violet), C (black), H (grey), O (red) and F (green).

Results and discussions

The adsorptions of the emerging contaminants, as well as of the interferents, were observed to be more favourable on metallic agglomerates than on organic

ligands (Table 1). The contaminants presented an adsorptive preference for pdw in comparison with pt. The triclosan showed the lower and the atrazine the higher adsorption affinity with the evaluated MOFs subunits. The water molecules only could not significantly compete with the adsorption of the emerging contaminants in the case of pdw subunit. Moreover, the other species Cl⁻, HSO₄⁻ and H₂PO₄⁻ were identified as important interferences to the pollutants remotion from water.

Table 1. The Gibbs free energy variation (ΔG) at 298 K for the adsorption processes of emerging contaminants and interfering species in the subunits of MOFs.

Species	$\Delta G / \text{kcal mol}^{-1}$			
	pdw	pt	H ₂ BDC	H ₃ BTC
Atrazine (a)	-11.01	7.45	3.32	2.61
Atrazine (b)	-15.70	-7.65	*	*
Caffeine (a)	-6.96	-5.19	2.88	1.89
Caffeine (b)	-10.42	-4.59	*	*
Triclosan (a)	-7.39	10.40	4.03	2.37
Triclosan (b)	7.18	9.73	*	*
H ₂ O	-5.87	-7.74	5.04	5.71
Cl ⁻	-59.80	-56.69	-19.77	-23.57
HSO ₄ ⁻	-41.28	-32.43	1.34	-0.29
H ₂ PO ₄ ⁻	-38.42	-43.97	0.53	-0.85

(a) and (b) indicate different forms to the coordination of contaminants in the subunits. * There is no data.

Conclusions

The comparison between the two kinds of subunits which constitutes the MOFs indicated that the preferential adsorption site might be localized at the metallic agglomerates. Furthermore, it was observed a better performance from the pdw than the pt subunit. Therefore, in the design of MOFs with adjusted properties for the remotion from water of the evaluated emerging contaminants, the most suggested subunit is pdw. In order to better understand the contribution of the MOFs composition in the process, it is also necessary to study the performance of the metallic agglomerates formed by other metals.

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Dihydrogen-Bonded complexes $\text{LiH}\cdots\text{HX}$ with $\text{X}=\text{F}, \text{Cl}, \text{CN}$ and CCH : QTAIM analysis and SAPT partitioning.

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Keywords: Dihydrogen-Bonds, QTAIM, SAPT.

INTRODUCTION

Dihydrogen-bonds (DHB) interaction can be considered a particular case of hydrogen bonds, occurring when hydrides ($\text{H}^\delta-$) interacts with protons ($\text{H}^{\delta+}$), and can be generally designated as $\text{MH}^{\delta-}\cdots{}^{\delta}\text{HX}$, where M is a metal or boron¹. The aim of this work was to analyze the $\text{H}\cdots\text{H}$ interaction in the $\text{LiH}\cdots\text{HX}$ complexes (with $\text{X}=\text{F}, \text{Cl}, \text{CN}$ or CCH) through the Quantum Theory of Atoms in Molecules (QTAIM) and energy decomposition from the Symmetry-Adapted Perturbation Theory (SAPT).

METHODS

The geometry of the $\text{LiH}\cdots\text{HX}$ complexes were fully optimized at the B3LYP/6-311++G(d,p) level of theory with all calculations carried out Gaussian 03 program². The QTAIM calculations were performed using the AIM2000 1.0, AIMStudio 17.01.25 and AIMQB 17.01.25. The SAPT partitioning were computed using Psi4 1.1 program.

RESULTS

Values of intermolecular distance and topological parameters are listed in Table 1. The $\text{LiH}\cdots\text{HCl}$ complex presented the lowest intermolecular distance ($R_{(\text{H}\cdots\text{H})}$) values as well as the highest electronic density ($\rho_{(\text{H}\cdots\text{H})}$) value, being the strongest bound in structural and topological terms. Regarding the QTAIM analysis, the $\text{H}\cdots\text{H}$ bond in the $\text{LiH}\cdots\text{HCl}$ complex can be considered covalent with a negative value of Laplacian ($\nabla^2\rho_{(\text{H}\cdots\text{H})}$). This interaction in the $\text{LiH}\cdots\text{HF}$ complex presents only a partial degree of covalence with $\nabla^2\rho_{(\text{H}\cdots\text{H})}>0$ and $1>(-\text{G}/\text{V}_{(\text{H}\cdots\text{H})})>0.5$, while complexes $\text{LiH}\cdots\text{HCN}$ and $\text{LiH}\cdots\text{HCCH}$ do not show any degree of partial covalence. Relationships between electron density and $R_{(\text{H}\cdots\text{H})}$ values were found, as can be seen in Figure 1 (1).

Tabela 1. Structural parameters and topological descriptors of the $\text{LiH}\cdots\text{HX}$ complexes.

Complexes	$R_{(\text{H}\cdots\text{H})}$	$\rho_{(\text{H}\cdots\text{H})}$	$\nabla^2\rho_{(\text{H}\cdots\text{H})}$	$-\text{G}/\text{V}_{(\text{H}\cdots\text{H})}$
$\text{LiH}\cdots\text{HF}$	1,346	0,048	0,047	0,670
$\text{LiH}\cdots\text{HCl}$	1,191	0,076	-0,025	0,446
$\text{LiH}\cdots\text{HCN}$	1,771	0,020	0,039	1,074
$\text{LiH}\cdots\text{HCCH}$	2,010	0,012	0,026	1,194

The electronic energy components (electrostatics (E_{elst}), dispersion (E_{disp}), exchange (E_{exch}) and induction (E_{ind})) inherent to the SAPT formalism are showed in a bar graphs presented in Figure 1 (2). For the complex with $\text{X}=\text{Cl}$ the induction component is the main attractive term, typical of covalent bonds, while for the other complexes the electrostatic component is dominant.

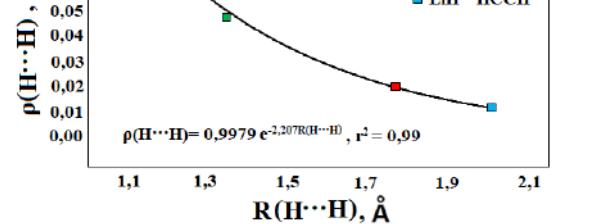


Figure 1. Relationships between intermolecular distance and electronic density (1) and SAPT results (2).

CONCLUSION

The structural analysis together with the QTAIM topology and the SAPT energy decomposition showed that the $\text{LiH}\cdots\text{HCl}$ complex is the most strongly bounded, with the $\text{H}\cdots\text{H}$ interaction being considered a covalent bond. Furthermore, the interaction strength showed the following trend: $\text{LiH}\cdots\text{HCl} > \text{LiH}\cdots\text{HF} > \text{LiH}\cdots\text{HCN} > \text{LiH}\cdots\text{HCCH}$.

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Enhancing NMR Quantum Computation by Exploring Heavy Metal Complexes as Multiqubit Systems: A Theoretical Investigation

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Keywords: *NMR parameters, quantum computation, qubit molecules.*

Introduction

Quantum computers could one day provide breakthroughs for some of today's unsolvable problems in areas such as chemistry and artificial intelligence.¹

Finding a suitable candidate for a quantum bit (qubit) is the major challenge for the physical implementation of quantum information processing (QIP), as well as bringing them together in an organized, scalable, and addressable way to implement the quantum gates.^{3,4}

A class of compounds, which could fulfill the requirements for NMR-QIP (large differences in the chemical shift of the involved nuclei and large spin-spin coupling constants (SSCCs) between them), are metal complexes with phosphine chalcogenide ligands, in the following abbreviated as MRE, of the type $MCl_2(R_3PE)_2$ with $M = Cd$ or Hg , $R = n\text{-Bu}$ or (Me_2N) , and $E = Se$ or Te (Figure 1).

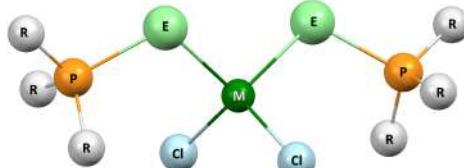


Figure 1 Metal complex with MRE of the type $MCl_2(R_3PE)_2$ ($M = Cd$ or Hg ; $R = n\text{-Bu}$ or (Me_2N) ; $E = Se$ or Te).

Assembled together with the most common qubits used in NMR quantum computation experiments, spin-1/2 nuclei, such ^{113}Cd , ^{199}Hg , ^{125}Te and ^{77}Se could leverage the prospective scalable quantum computer architectures, enabling many and heteronuclear qubits for NMR quantum information processing implementations.

Computational details

A computational design strategy for prescreening recently synthesized complexes of cadmium, mercury, tellurium, selenium and phosphorus (called MRE complexes) as suitable qubit molecules for NMR QIP is reported. Chemical shifts and spin-spin coupling constants in five MRE complexes were examined using the spin-orbit zeroth order regular approximation (ZORA) at the density functional theory (DFT) level and the four-component relativistic Dirac-Kohn-Sham approach.

Results and conclusion

In particular, the influence of different conformers, basis sets, exchange-correlation functionals and methods to treat the relativistic as well as solvent

effects were studied. The differences in the chemical shifts and spin-spin coupling constants between different low energy conformers of the studied complexes were found to be very small. The TZ2P basis set was found to be the optimum choice for the studied chemical shifts, while the TZ2P-J basis set was the best for the couplings studied in this work. The PBE0 exchange-correlation functional exhibited the best performance for the studied MRE complexes. The addition of solvent effects has not improved on the gas phase results in comparison to experiment, except for the phosphorus chemical shift. The use of MRE complexes as qubit molecules for NMR QIP could face the challenges in single qubit control and multiqubit operations (Table 1). They exhibit chemical shifts appropriately dispersed, allowing qubit addressability and exceptional large spin-spin couplings, which could reduce the time of quantum gate operations and likely preserve the coherence.

Table 1 Differences in the Larmor Frequencies (for a 10 T Magnet) between the M (^{113}Cd or ^{199}Hg) nucleus and ^{31}P or between the E (^{77}Se or ^{125}Te) nucleus and ^{31}P , $\Delta\nu$ [MHz] and $M-P$ ($M = ^{113}Cd$ or ^{199}Hg), and $E-P$ ($E = ^{77}Se$ or ^{125}Te) SSCCs, J [Hz] calculated using the two-component ZORA^a

	$\Delta\nu$ ($M-P$)	$^2J_{M-P}$	$\Delta\nu$ ($E-P$)	$^2J_{E-P}$
CdBuTe	78.0	39.4	37.6	1525
CdMeTe	78.0	46.6	37.6	2041
CdMeSe	78.0	37.3	91.1	-845
HgBuTe	96.2	-137	37.5	1512
HgMeTe	96.2	-169	37.5	2045

^aAll calculations were carried out with the PBE0 exchange-correlation functional and the TZ2P basis set, where in the case of the ZORA SSCC calculations ZORA-JCPL basis set was employed. For atoms in similar chemical environments, the average chemical shifts and SSCCs are reported.

Conclusion

The use of MRE complexes as qubit molecules for NMR QIP could face the challenges on single qubit control and multiqubit operations, broadening the forthcoming scalable quantum computer.

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Nanoestruturas de carbono e halobenzoquinonas: um estudo *ab initio*.

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Keywords: *Nanoestruturas de carbono, Halobenzoquinona, DFT*.

Introdução: Ao longo dos anos a natureza vem sofrendo por conta da grande quantidade de poluentes ocasionados pela ação do homem, surge a necessidade de desenvolver processos para identificar e remover estes poluentes. Uma possível solução para a remoção ou detecção dessas substâncias tóxicas do meio ambiente é utilizar as nanoestruturas de carbono que hoje são vistas como possíveis filtros ou sensores de substâncias tóxicas (CASTRO et al., 2017). **Objetivo:** Estudar as propriedades eletrônicas e energéticas da interação do grafeno e fulereno com halobenzoquinonas (HBQs). **Metodologia:** Cálculos de primeiros princípios baseados na Teoria do Funcional da Densidade (DFT) (HOHENBERG; KOHN, 1964) por meio do programa computacional SIESTA. **Resultados e Discussão:** Os resultados da interação da HBQs 2,6-dibromo-1,4-benzoquinona adsorvida na superfície do grafeno ocorre através de um processo físico, enquanto que a interação com fulereno ocorre através de processo químico. **Conclusão:** As análises das propriedades estruturais, energéticas e eletrônicas mostram que é possível a utilização dessas duas nanoestruturas como filtros para esse poluente. Dessa forma podemos confirmar, por meio de simulações computacionais, a utilidade do grafeno e fulereno como filtros para futuras aplicações.

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Obtenção dos potenciais de oxidação e pKa teóricos de complexos de cobalto homolépticos com ligantes N-heterocíclicos

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Palavras-Chave: Cobalto, pKa, Oxidação.

Introdução

Os cálculos de estrutura eletrônica de vários complexos homolépticos de cobalto em diferentes estados formais de oxidação (II, III e IV) com os ligantes N-heterocíclicos 2-(1H-imidazol-2-yl)-pyridine (Himpy), 2-(1H-imidazol-2-yl)-pyrimidine (Himpm), 2-(1H-imidazol-2-yl)-pyrazine (Himpz) e 2-(1H-imidazol-2-yl)-pyridazine (Himpa) foram avaliados. Por meio das energias livres de Gibbs de solvatação, foram calculados os valores de pKa de cada complexo nos diferentes estados de oxidação. Os potenciais de oxidação também foram obtidos para todos os complexos em diferentes estados de protonação.

Metodologia

Todos os cálculos foram realizados usando o software ORCA (4.2.0).¹ O modelo empregado consistiu na utilização do funcional híbrido PBE0 e def2-SVP como conjunto de bases.^{2,3} Para contabilização dos efeitos do solvente, utilizou-se o método C-PCM.⁴ Todos os valores de pKa e potenciais foram obtidos através das estruturas otimizadas. Os valores de pKa foram calculados por meio da estratégia isodésmica usando o ácido fórmico/ formiato como valor de pKa experimental padrão para uma série de ligantes N-heterocíclicos com pKa conhecidos.⁵ Os potenciais para todos os estados de protonação dos complexos foram calculados utilizando $E^\circ(H^+/H_2)_{abs} = 4.281$ V como potencial padrão absoluto para o eletrodo de hidrogênio em água.⁶

Resultados

Após a obtenção de todos os potenciais de oxidação referentes aos pares Co(II)/Co(III) e Co(III)/Co(III)L* para cada estado de protonação, foram construídos diagramas de Pourbaix (figura 1). Por meio das densidades de spin obtidas foi possível observar que a 1º oxidação ocorre no centro metálico, ao passo que a 2º oxidação ocorre no ligante. Para os pares Co(II)/Co(III), as estruturas completamente protonadas apresentaram os maiores potenciais de oxidação, sendo que a medida que prótons foram retirados, esses potenciais se tornaram cada vez mais negativos devido ao acúmulo de carga negativa no centro

metálico. Os complexos com os ligantes Himpy apresentaram os menores potenciais de oxidação como esperado devido ao menor efeito indutivo desse ligante sobre o centro metálico. Para o par Co(III)/Co(III)L* os potenciais de oxidação obtidos foram mais altos em relação ao primeiro par, uma vez que o elétron retirado está sob influência de um maior potencial eletrostático. Os valores de pKa são menores para os complexos Co(III) em relação ao Co(II), como esperado.

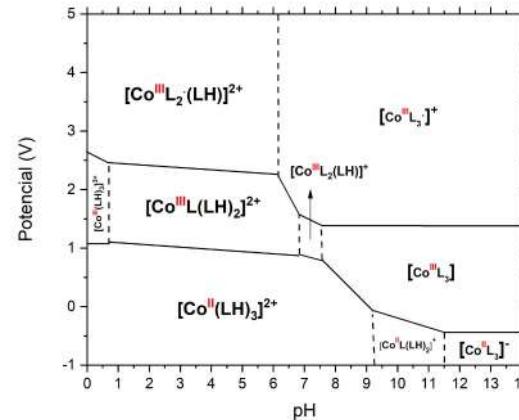


Figura 1: Diagrama de Pourbaix do fac-Co(Himpy).

Conclusão

Este trabalho mostra a importância do design de ligantes evidenciando como é possível modular certas propriedades dos complexos por meio de alterações na esfera de coordenação.

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Modelagem da interação do radical hidroxil com o 1,4-dioxano.

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Palavras-Chave: degradação, radical hidroxil, 1,4-dioxano.

Introdução

O 1,4-dioxano é um composto de éter cíclico sintético muito utilizado como um agente estabilizante em diversos produtos químicos¹. Porém, ele foi classificado pelo Departamento de Saúde e Serviços Humanos (DHHS) como um potencial agente carcinogênico para humanos. Dessa forma, diversos estudos relacionados à remediação do 1,4-dioxano estão em desenvolvimento pela comunidade científica².

Nas últimas décadas, os Processos Oxidativos Avançados – POAs – vêm ganhando espaço nas pesquisas relacionadas ao tratamento de água com ênfase na remoção de compostos orgânicos, principalmente compostos que apresentam alta toxicidade e baixa degradabilidade³.

Assim, este trabalho objetiva modelar a reação de abstração inicial do átomo de hidrogênio do 1,4-dioxano promovido pelo radical hidroxil.

Metodologia

As propriedades eletrônicas das estruturas estacionárias da primeira interação do 1,4-dioxano com o radical hidroxil, apresentado na Figura 1, foram calculados utilizando o nível de cálculo MP2/6-311G+(d) juntamente com o modelo de solvatação contínuo (SMD) para simular o meio aquoso para a reação.

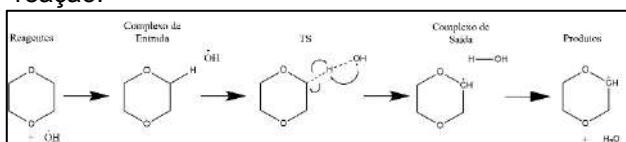


Figura 1 - Interação do radical hidroxil com o 1,4-dioxano.

Durante os cálculos eletrônicos foram também determinadas as frequências vibracionais das espécies, a fim de caracterizar as estruturas otimizadas como mínimos locais ou estados de transição.

Resultados

Após os cálculos das estruturas eletrônicas, as contribuições de energia vibracional do ponto zero foram consideradas para se montar o perfil enérgico da reação de abstração do átomo de hidrogênio do 1,4-dioxano, mostrado na Figura 2.

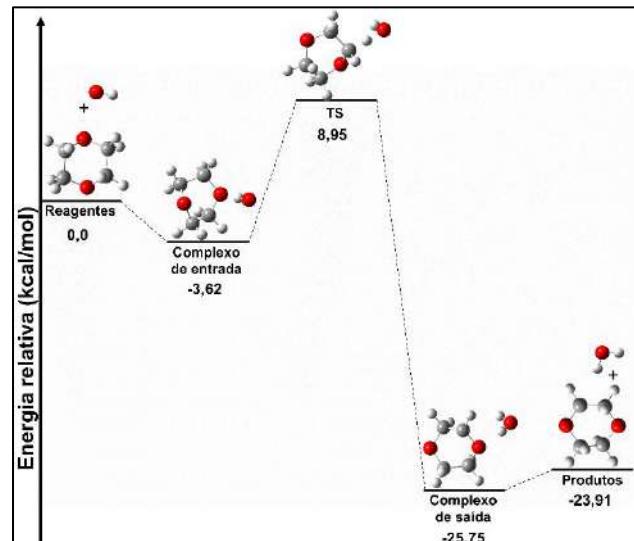


Figura 2 - Perfil de energia relativa correspondente à abstração inicial do átomo de hidrogênio do 1,4-dioxano.

A reação é energeticamente favorecida, apresentando caráter exotérmico. Devido à alta reatividade do radical hidroxil, a barreira de reação apresenta um valor relativamente baixo, indicando, assim, a viabilidade cinética da ocorrência da reação de abstração do hidrogênio.

Conclusão

Este trabalho constatou que o radical hidroxil é capaz de promover a abstração de um hidrogênio da estrutura do 1,4-dioxano, cuja barreira de ativação é de 8,95 kcal/mol. Essa abstração do hidrogênio é a primeira etapa do mecanismo de degradação do 1,4-dioxano promovido pelo radical hidroxil.

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Agradecimento





Theoretical study of the surface structure, morphology, and photocatalytic activity of Ag₂O

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Palavras-Chave: DFT, Structure-activity relationships, Photocatalysis.

INTRODUCTION

A precise understanding of the morphology of semiconductor materials is critical to identify the correlations between crystalline structure, activity, and technological applications; the latter can be improved and stabilized by tailoring the surface structures and exposed crystal faces of the material [1]. In this context, Silver oxide (Ag₂O) bulk based on explicit and realistic models has been investigated to explain the wide connection between morphology, electronic structure, and photocatalytic properties, rationalizing the experimental results and understand the origin of the photoactivity by identifying the nature of the photo-induced carriers and the shape-dependent photocatalytic mechanism [2].

METHODOLOGY

Density functional theory (DFT) calculations were performed within the linear combination of atomic orbitals approach, as implemented in the CRYSTAL14 [3] code and B3LYP hybrid functional. The analyses of the electronic properties in terms of Density of States (DOS) projections, band structure profiles, and electronic density distributions. The pristine cubic (Pn-3m) unit cell was modeled by two Ag₂O unit formulas (six atoms). Neutral (V_O^x and V_{Ag}^x) and charged (V_O⁻, V_O⁺ and V_{Ag}⁻) vacancies were modeled by embedding them in 2×2×2 Ag₂O supercells containing 48 atoms. The (hkl) crystalline plane of interest, cut from the optimized bulk geometry of the selected were (100), (110), and (111) surfaces.

RESULTS AND DISCUSSIONS

The theoretical results reveal the electronic structure of both pure and defective Ag₂O, indicating that photo-generated e⁻ and h⁺ exhibit distinct paths for mobility along of different crystallographic directions. In particular, (100) and (110) planes show the highest carrier stabilization, due to the increased ratio between the effective masses of e⁻ and h⁺. It was proved that both neutral and charged V_{Ag} defects shows a favorable influence on the photocatalytic behavior of Ag₂O once the recombination rate between electrons and holes increased. Different morphologies were constructed by tuning the E_{surf} values for the (100), (110), and (111) surfaces (Figure 1), and were found in excellent agreement with the experimental results.

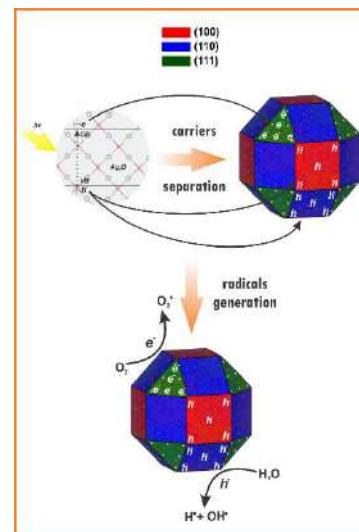


Figure 1. Schematic representation of the photocatalytic mechanism in shape oriented Ag₂O materials.

On the other hand, the two low-energy (100) and (010) surfaces are dominant in the Wulff shape. The high surface energy and the obvious surface relaxation of the Ag₂O (001) surface indicate its high photocatalytic activity, which is in accordance with other experimental results.

CONCLUSIONS

Combined with the results of previous photocatalytic experiments, we found how Ag₂O crystals with exposed (100) and (110) surfaces enhance the photocatalysis process, enabling the photo-generated carriers to be used for effectively generate radical species. A combination of different theoretical tools allowed us to understand the nature of the superior photocatalytic behavior of some Ag₂O morphologies, and thus represents an interesting protocol to investigate other semiconductor photocatalysts.

ACKNOWLEDGEMENTS

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OLEDs of DCM2-doped Alq3: the emission redshift caused by nonlinear Stark effect and Förster mediated exciton diffusion

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Keywords: OLEDs, DCM2-doped Alq3, Stark Effect, Emission Redshift.

Organic light-emitting diodes (OLEDs), devices in the archetype small-molecule fluorescent guest-host system tris(8-hydroxyquinolinato) aluminum (Alq3) doped with 4-(dicyanomethylene)-2-methyl-6-julolidyl-9-enyl-4H-pyran (DCM2) displays a redshift in light-emission frequency which is extremely sensitive to the dopant concentration [1]. This effect can be used to tune the emission frequency in this particular class of OLEDs [1]. In this work, a model is proposed to describe this effect using a combination of density functional theory, quantum-chemical calculations and stochastic simulations of exciton diffusion via a Förster mechanism [2]. The results show that the permanent dipole moments of the DCM2-doped Alq3 matrix generate random electric fields that are large enough to cause a nonlinear Stark shift in the band gap of neighboring DCM2 molecules (Fig. 1A). As a consequence of these nonlinear shifts, a non-Gaussian probability distribution of highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO-LUMO) gaps for the DCM2 molecules in the Alq3 matrix is observed (Fig. 1B), with long exponential tails to the low-energy side. Surprisingly, this probability distribution of DCM2 HOMO-LUMO gaps is virtually independent of DCM2 concentration into the Alq3 matrix, at least up to a fraction of 10% [2]. This study shows that the distribution of gaps, combined with out-of-equilibrium exciton diffusion among DCM2 molecules causes a thermalization in exciton energy (Fig. 1C), which results in the emission redshift[2]. The theoretical results obtained in this work showed to be in agreement with the experimental results already existing in the literature.

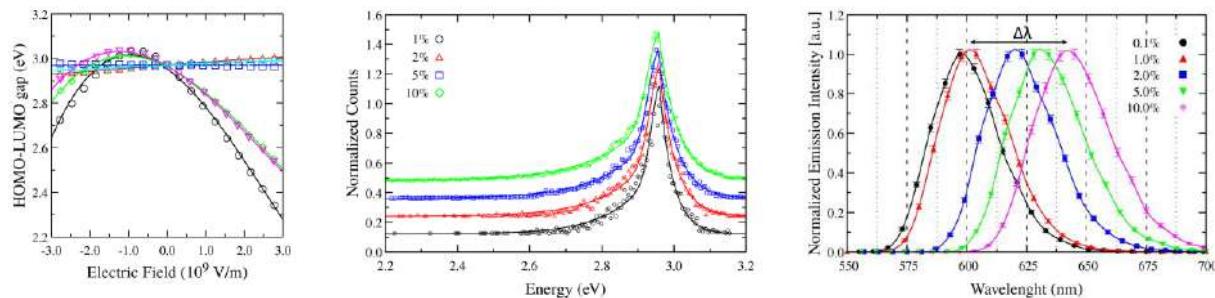


Figure 1: (A) Nonlinear Stark shift in the band gap of DCM2 caused by resulting electric fields in the system. (B) Non-Gaussian probability distribution for DCM2-doped Alq3 matrix. (C) Theoretical redshift emission obtained for DCM2-doped Alq3 matrix.

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Brønsted Acid Catalyzed Methoxy to Hydroxy Rearrangements in Isoquinoline Compounds

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Palavras-Chave: Isoquinoline, Brønsted Acid, DFT-D3, SMD.

Introduction

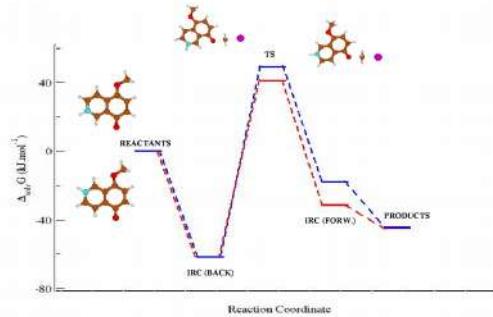
Isoquinoline is a structural isomer of quinolin, heterocyclic aromatic organic compounds. It is composed of a benzene ring fused to a pyridine ring (benzopyridines). The term isoquinoline is used to make reference to isoquinoline derivatives. These derivatives are a large class of medically active alkaloids with very varied properties: anti-inflammatory, antifungal, antitumor, antimicrobial, and antiviral to analgesic. In this work we have studied the Brønsted acid catalyzed methoxy to hydroxy in 5,8-dimethoxy isoquinoline.

Computational Details

Electronic and molecular structures of compounds originated from the reaction between Brønsted acid and 5,8-dimethoxy isoquinoline were investigated through theoretical calculations. The calculations were performed using DFT and employing the hybrid exchange-correlation functional (B3LYP). Geometry optimizations and evaluation of harmonic frequencies were performed at the B3LYP/6-311++G(2d,p) level of theory. The optimized structures were confirmed to be minima by vibrational frequency analysis. The single point energy calculations were carried out at B3LYP/6-311++G(3df,2p) level on corresponding optimized geometries. The solvent effects (for water) were included using the SMD solvation model. The dispersion corrections were included using semiempirical atom pairwise interactions. DFT-D3 method developed by Grimme *et al* was employed because this methodology has been shown to give quite accurate thermochemistry for both covalently bonded systems and systems containing dispersion forces. All computations were performed using the Gaussian 09 D.01 quantum chemistry package.

Results and Discussion

At Fig.1 can be observed the reaction coordinate from 5,8-dimethoxy isoquinoline (**Reactants**). In first step HBr(aq) transfers a proton to N atom (**IRC (BACK)**). Then the bromine anion attacks, either the methoxy group at 5 position or at 8 position. These structures are described by transition states, **TSa**, -467.53 cm⁻¹ or **TSb**, -451.07 cm⁻¹, respectively. These transition states forward to the formation of structures **IRC(FORW.)**, where the first compound has the deprotonated oxygen at 8 position and the second at 5 position, respectively, and CH₃Br. In the final step, the new proton transfer takes place. It occurs between the hydrogen bonded the nitrogen atom and these oxygen atoms. The final products are: 5-hydroxy-8-methoxy isoquinoline and 8-hydroxy-4-methoxy isoquinoline (structures **PRODUCTS**, respectively). The 5-hydroxy-8-methoxy isoquinoline is more stable than 8-hydroxy-4-methoxy isoquinoline. These calculations are in agreement with experimental results.



Acknowledgment

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Avaliação de regressão multilinear empregando a reação direta para a previsão do pKa de ácidos e aminas

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Palavras-Chave: Previsão de pKa, Regressão

Introdução

O pKa caracteriza-se como uma propriedade importante para diversas aplicações. Logo, algoritmos computacionais que realizam estimativas acerca desta grandeza vêm sendo intensivamente pesquisados.^{1,2} Dentre as várias alternativas disponíveis surgem as metodologias estatísticas. O princípio fundamental desta metodologia se resume na construção de modelos que correlacionam o pKa com um ou mais parâmetros que contenham informações estruturais/energéticas do ácido e sua base conjugada.³

Partindo destes pressupostos, define-se como objetivo deste trabalho avaliar o desempenho de um modelo de regressão para a previsão de pKa.

Metodologia

Neste trabalho o pKa foi representado como uma função multilinear envolvendo a energia livre do ácido e de sua base conjugada, empregando 3 parâmetros:

$$pKa = a + b \cdot G_{soln}(A^-) + c \cdot G_{soln}(AH)$$

Sendo a , b e c parâmetros ajustáveis determinados por regressão minimizando o erro em relação a valores de pKa experimentais. As moléculas escolhidas totalizam 50 ácidos e 40 aminas com grande diversificação estrutural. Metade dos compostos foram considerados para o conjunto de treinamento e a outra metade para o conjunto de validação. Os cálculos foram efetuados de acordo com o seguinte esquema:

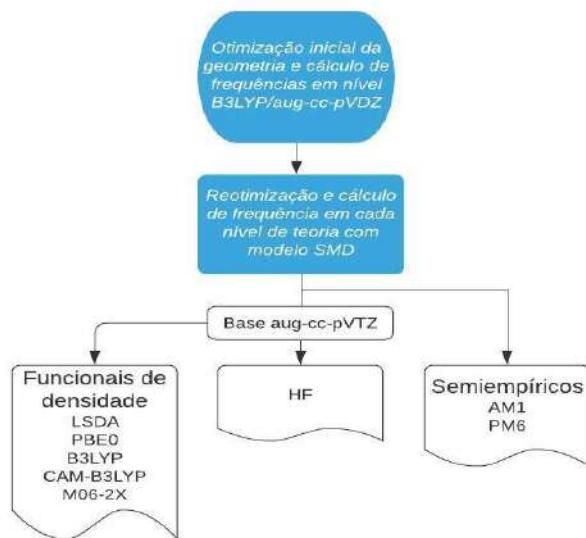


Figura 1: Esquema de cálculo

Resultados

A Figura 2 mostra os resultados para cada grupo de moléculas:

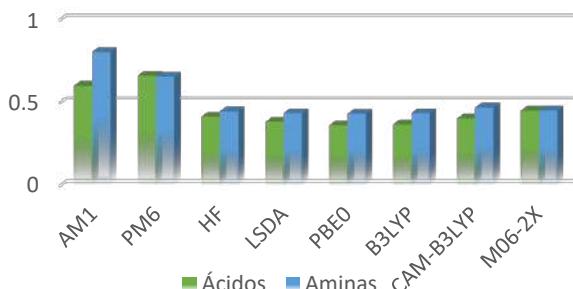


Figura 2: Desvios absolutos médios para cada nível de teoria em unidades de pKa

Como pode ser observado todos os valores são inferiores a uma unidade de pKa, indicando um excelente desempenho para os grupos funcionais estudados. Os métodos semiempíricos surpreendentemente apresentam bons resultados dentro do modelo proposto para a previsão de pKa. Observa-se que o método HF mesmo não contendo contribuições de correlação eletrônica é capaz de fornecer estimativas de pKa tão boas quanto cálculos DFT, que apresentam um excelente desempenho. Mesmo funcionais locais, PBE0 e LSDA, fornecem excelentes resultados.

Conclusões

Desenvolveu-se um modelo de regressão para cálculo de pKa baseada na reação direta. Em todas as condições testadas os desvios absolutos obtidos foram inferiores a uma unidade de pKa. O funcional PBE0 apresentou o melhor desempenho em relação aos métodos testados. Os excelentes resultados indicam uma boa aplicabilidade do modelo nos grupos funcionais testados.

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Agradecimentos

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XXI SBQT

Azlactone Dynamic Kinetic Resolution Catalyzed by Chiral Phosphoric Acids: Mechanism and Origin of the Enantioselectivity

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Palavras-Chave: Azlactone, Dynamic Kinetic Resolution, Enantioselectivity.

INTRODUCTION

Azlactones are versatile five-membered heterocycles widely employed in a diversity of transformations, in special dynamic kinetic resolution reaction (DKR) through ring-opening in the presence of nucleophiles (alcohols, amines).¹ The use of chiral Brønsted acids as catalysts for this transformation is still underdeveloped, with only two described protocols, with limitations concerning the control of the stereochemical outcome of the products.^{2a,2b} In this context, a better comprehension of the reaction mechanism, as well as of the key interactions responsible for the enantioselectivity is highly desirable.

RESULTS

The calculations were performed using the Gaussian 09 package,³ the density functional theory (DFT) at the M06-2X/6-31++G(d,p)//M06-2X/6-31G(d) level of theory and the solvation model based on density (SMD) for chloroform or toluene.

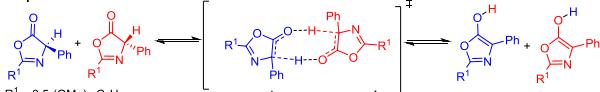
The DKR of azlactones consists of two steps: a rapid isomerization of the substrate, followed by the ring-opening by the nucleophile. Three plausible proposals involving the isomerization step were investigated (Scheme 1), with the most viable proposal involving a Münchnone-type intermediate (proposal 3 - $\Delta G^\ddagger = 14.31$ to 14.64 kcal mol⁻¹). NMR control experiments were also carried out and corroborated with this proposal.

Next, the ring-opening step by alcoholysis was investigated using a single-step model and applied in

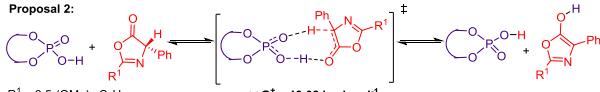
a diversity of previously described experimental conditions (Table 1). It is worth mentioning that the selected conditions were challenging, and involved drastically decreases in the e.e. or even the inversion of the major enantiomer being formed (entries 2 and 3). Notably, the developed model was successfully applied, allowing the accurate prediction of the enantiomeric excesses, with errors of only 0.20 to 0.26 kcal mol⁻¹. The DKR through aminolysis (which not only alters the nucleophile, but also the solvent and catalyst) was also successfully predicted (entry 4). Complementary analysis were carried out to shed light on the origin of the enantioselectivity, such as the distortion/interaction activation strain analysis and the analysis of non-covalent interactions (NCI) using NCI plot. The results revealed that both interaction (mainly due to NCI) and distortion terms contributes towards the computed $\Delta\Delta G^\ddagger$.

Scheme 1. Investigated azlactone isomerization mechanisms.

Proposal 1:



Proposal 2:



Proposal 3:

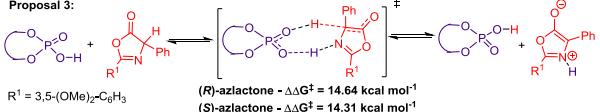
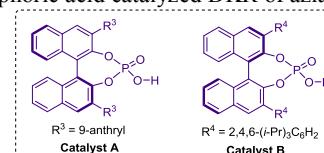
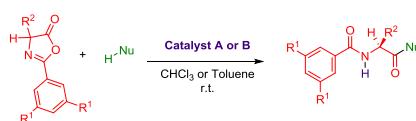


Table 1. Investigated protocols concerning the phosphoric acid catalyzed DKR of azlactones.



Entry	R ¹	R ²	Nu-H	Catalyst	ΔG^\ddagger (kcal mol ⁻¹)	Predicted e.e. (%)	Experimental e.e. (%) ^a	Error (kcal mol ⁻¹)
1	OMe	Ph	1-Naphthyl-CH ₂ OH	A	2.10	94	-91 ^b	0.26
2	OMe	Ph	MeOH	A	1.19	76	-68 ^b	0.20
3	OMe	Me	1-Naphthyl-CH ₂ OH	A	-0.33	-27	8 ^b	0.23
4	H	Ph	PhNH ₂	B	0.94	66	37	0.47

^a Data from references 2a and 2b; ^b Reaction carried out with the opposite catalyst.

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ACKNOWLEDGMENT

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Interações do dímero de água com naftaleno: Implicações da microssolvatação nos espectros vibracionais e na cinética de reorientação intermolecular

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Palavras-Chave: *Ligações de Hidrogênio, Interações de Van der Waals, Espectro vibracional, Cinética de reorientação.*

INTRODUÇÃO

As interações formadas entre hidrocarbonetos aromáticos policíclicos (PAH's) e aglomerados de água têm despertado interesse tanto na compreensão de seus aspectos fundamentais, como no entendimento da microssolvatação de PAH's em baixas temperaturas. Uma das motivações do interesse é a suspeita de que tais interações estejam envolvidas no início da formação de gelo em ambientes interestelares^{1,2}. Além disso, atribui-se que algumas bandas de emissão na região do infravermelho em nuvens interestelares observadas em algumas galáxias são devidas a presença de moléculas de PAH's, compondo a fase gasosa, como foi confirmado em estudos recentes³.

No presente estudo, investigamos complexos neutros formados entre um dímero de água e o naftaleno. Analisamos os aspectos estruturais, energéticos, vibracionais e cinéticos dos complexos intermoleculares.

MÉTODOS

Utilizamos métodos perturbativos e a teoria do funcional da densidade (DFT), no âmbito de funcionais híbridos e de correções de vdW. O conjunto de funções de base usado foi o 6-311++G(d,p) para os níveis de cálculo, realizados com os programas Gaussian 09 e 16. A cinética reorientacional foi investigada no contexto da teoria do estado de transição (TST), usando o programa Pilgrim.

RESULTADOS

As estruturas de mínima energia encontradas mostram que o dímero de água interagem com a molécula de naftaleno por interações do tipo O-H···π e C-H···O como mostrado na figura 1.

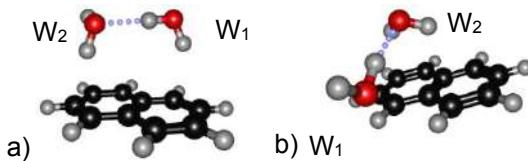


Figura 1. Geometrias otimizadas do complexo naftaleno-dímero de água: a) estrutura 1 e b) estrutura 2.

Na estrutura 2, as ligações O-H···O são mais favorecidas, o que torna a estrutura energeticamente mais estável quando comparada a estrutura 1. A análise vibracional indica, na região acima de 3500

cm⁻¹, desvios para o vermelho nos modos de estiramento das ligações O-H. Na região entre 200 e 800 cm⁻¹ observamos bandas relativas aos modos de dobramento, torção e estiramento dos anéis aromáticos e de vibrações C-C e C-H fora do plano. Também observamos modos acoplados da molécula de naftaleno e modos intermoleculares do dímero de água.

No espectro Raman, os modos mais ativos são os de estiramento dos anéis aromáticos da molécula de naftaleno, os quais possuem intensidades relativamente baixas ($> 50 \text{ \AA}^4 \text{ amu}^{-1}$) e baixas taxas de despolarização (< 0.40).

O modelo proposto para a cinética de reorientação do dímero de água é de regime unimolecular e de baixa barreira. A faixa de temperatura considerada foi de 5 a 300 K. O esquema é mostrado na figura 2.

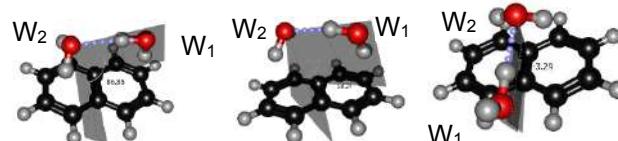


Figura 2. Reorientação do dímero de água sobre a molécula de naftaleno.

Os valores das constantes cinéticas sugerem que em baixas temperaturas a reorientação ocorre lentamente e tem valores maiores na direção dos produtos (estrutura 2). Em temperaturas próximas a do ambiente, os valores das constantes cinéticas são relativamente altos e sugerem um equilíbrio termodinâmico em que as populações das estruturas 1 e 2 são semelhantes.

CONCLUSÕES

Os resultados sugerem que a estabilidade dos aglomerados em questão são consequência de um balanço entre as interações O-H···O, C-H···O e O-H···π.

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AGRADECIMENTOS

***In silico* investigation of Mg-MOF-74 as arsenic adsorbent in contaminated water.**

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Keywords: arsenic, MOFs, DFT.

Abstract

Arsenic is a highly toxic metal. The use of this element in anthropogenic activities, such as agriculture and mining, and its natural occurrence in the environment, are responsible for the arsenic contamination of water bodies. The arsenic contamination of water bodies is a relevant problem all over the world. Therefore, the World Health Organization (WHO) defined the solution as a priority matter as this metal is not withdrawn by conventional water treatment methods. Among the recently explored methods to remove this metal of water, there is adsorption[1], membrane technologies[2], bioremediation[3], and coagulation[4]. The adsorption techniques are a low-cost and easy operation option, which generate few subproducts and has a high turnover capacity[5]. With this in mind, the metal-organic frameworks (MOFs) are introduced as potential efficient materials for arsenic adsorption[6, 7, 8]. The MOFs are highly porous crystalline materials constituted by the Secondary Building Units (SBUs) composed of metallic clusters, and organic linkers. These parts combine three-dimensionally, forming pores with a large surface area, which are interesting for sorption applications[9].

In this work, we researched thermodynamic, structural, and electronic properties of the adsorption on Mg-MOF-74 (Figure 1) of common arsenic species found in water as follows: AsH₃, H₃AsO₃, H₃AsO₄, HAsO₂, HAsO₃, and CH₃H₂AsO₃. We compared the adsorption of these arsenic species with the adsorption of other usual components found in water, H₂SO₄, H₃PO₄, H₂O, NaCl, and HCl, to verify the capacity of Mg-MOF-74 adsorbing arsenic species against other molecules. We developed this study using the approach of the Density Functional Theory (DFT). The calculations were performed using periodic boundary conditions and plane waves as basis functions, implemented at *QuantumESPRESSO* software[10]. The theoretical level used in the simulations of this work was defined by De Oliveira *et al.*, 2018, using PBE/US pseudopotentials[11] and the Grimme correction[12] for dispersion interactions.

As preliminary results, we noticed that the adsorption of H₃AsO₄, HAsO₂, HAsO₃, and CH₃H₂AsO₃ is favorable when compared with the other molecules' adsorption. We also realized that the arsenic atom is not the preferential one for sorption. In species as AsH₃ and H₃AsO₃, where the adsorption occurred by

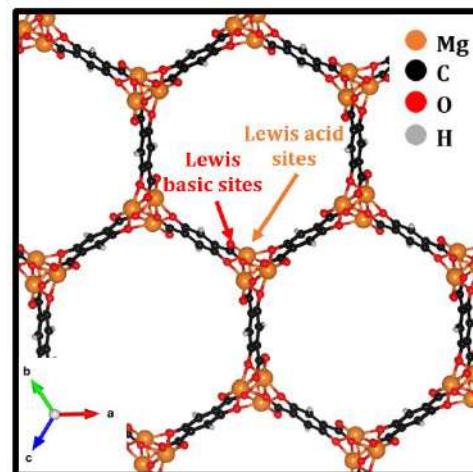


Figure 1: Indications of the Lewis basic and acid sites for adsorption at Mg-MOF-74.

the arsenic atom, the sorption was not as favorable as the adsorption of H₃AsO₄, HAsO₂, HAsO₃, and CH₃H₂AsO₃, which were adsorbed, preferably, by the oxygen atom.

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Desenvolvimento de parâmetros compatíveis com o campo de força CHARMM36 para clusters $[Fe_4S_4]^{2+}$ e simulações de dinâmica molecular da adenosina-5'-fosfossulfato redutase no GROMACS 2019

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Palavras-Chave: Adenosina-5'-fosfossulfato redutase dissimilativa, aglomerados $[Fe_4S_4]^{2+}$, parametrização de campo de força para simulações de dinâmica molecular.

Introdução

A adenosina-5'-fosfossulfato redutase (APSRAB) é uma metaloenzima que contém dois clusters $[Fe_4S_4]^{2+}$, vitais para a catálise¹. A falta de parâmetros confiáveis para essa espécie dificulta estudos de simulações de dinâmica molecular (MD) de sistemas contendo $[Fe_4S_4]^{2+}$. O objetivo deste trabalho foi obter parâmetros para $[Fe_4S_4]^{2+}$ a partir de cálculos da teoria do funcional de densidade (DFT) e validar esses parâmetros com simulações MD de dois sistemas APSRAB.

Metodologia

Cálculos DFT foram feitos em Gaussian 09² com o funcional/conjunto de base TPSSTPSS / DGTZVP no modelo $[Fe_4S_4(SCH_2CH_3)_4]^{2-}$ (**Figura 1**).

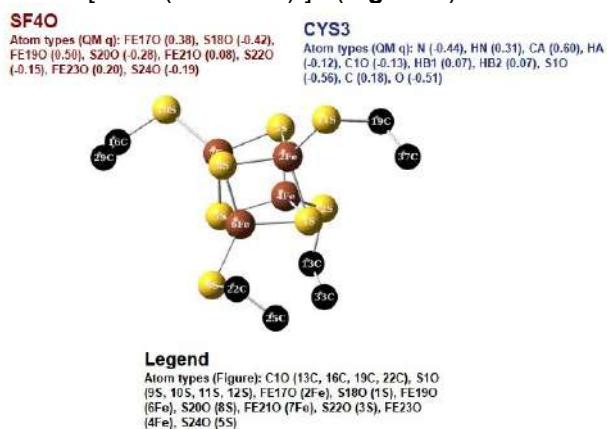


Figura 1. $[Fe_4S_4(SCH_2CH_3)_4]^{2-}$ calculado com TPSSTPSS/DGTZVP e átomos e cargas inseridas no campo de força.

Simulações MD de 50 ns foram feitas no pacote GROMACS 2019³. Os modelos 1JNR e 2FJD obtidos do Protein Data Bank (PDB) foram utilizados nas simulações.

Resultados

Dois novos resíduos foram adicionados ao campo de força: SF4O ($[Fe_4S_4]^{2+}$) e CYS3 (cisteínas que coordenam $[Fe_4S_4]^{2+}$) (**Figura 1**). A análise temporal dos parâmetros inseridos no campo de força esteve de acordo com os dados experimentais de difração de raios-X. A análise da evolução temporal dos sistemas estudados indicou que estes e, em

particular, os clusters nas respectivas cavidades apresentavam boa estabilidade e bom acordo com o observado em trabalhos anteriores (**Figura 2**).

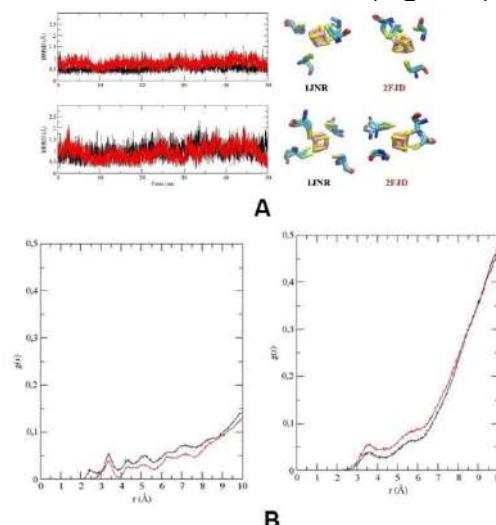


Figura 2. Séries temporais de RMSD (Root-mean-square difference, A) e RDF (Radial distribution function, B).

Conclusão

Os parâmetros obtidos fornecem a base para o estudo do APSRAB bem como de outros sistemas que contenham $[Fe_4S_4]^{2+}$ através do campo de força CHARMM36 usando o pacote GROMACS 2019.

Agradecimentos

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Docking molecular da bioatividade da Estavudina, Grazoprevir, Lamivudina, Oxifenisatina, Remdesivir, Rimantadina e Tenofovir contra a COVID-19.

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Palavras-chave: docking, protocolo, antivirais, covid-19

Introdução

A infecção por Covid-19 ocorre com o encaixe da proteína viral no receptor celular ACE-2 e a tradução de proteínas virais ocorre pela RdRp, na fase de pós-fusão; sendo importante analisar os complexos dos antivirais tanto com a proteína S quanto com os receptores celulares. Assim, esses receptores são alvos promissores para diferentes agentes terapêuticos¹. Vários protocolos clínicos têm sido adotados contra o SARS-CoV-2, incluindo o uso de Remdesivir, Gazoprevir, Tenofovir, Estavudina, Lamivudina, Oxifenisatina e Rimantadina²⁻³, que foram avaliados nessa pesquisa em docking molecular contra a Proteína S, a ACE-2 e a RdRp.

Materiais e Métodos

Três alvos virais diferentes foram considerados para o acoplamento, a Proteína Spike⁴, a Enzima ACE-2⁵ e a Polimerase RNA dependente de RNA⁶. Os ligantes foram otimizados com DFT. Os sítios ativos foram determinados usando o Atlas Computacional para Topografia de Superfície de Proteínas (CASTP) (<http://sts.bioe.uic.edu/castp/index.html?2011>) e Discovery Studio 2020. Após o docking foi escolhida a pose com maior afinidade de ligação e com o menor RMSD. O docking foi feito com o GOLD 2020, com o protocolo Chemscore/Goldscore.

Resultados e Discussão

Conforme a Tabela 1, tanto na fase de pré-fusão do vírus (proteína S e ACE-2) quanto na fase de pós-fusão (RdRp), a maioria dos antivirais estudados mostraram excelentes afinidades de ligação, demonstrando tanto a capacidade de impedir a infecção quanto de inibir os mecanismos de replicação do vírus após a entrada na célula, particularmente, em relação ao processo de produção de proteínas virais.

Tabela 1. Afinidade de ligação obtidas no docking.

Protocolo	Proteína S	ACE-2	RdRp
Estavudina	-17,09	-19,18	-13,71
Grazoprevir	-27,92	-26,81	-19,66

Lamivudina	-19,61	-17,19	-14,22
Oxifenisatina	-25,58	-22,31	-16,95
Remdesivir	-24,39	-13,94	-12,22
Rimantadina	-28,90	-26,59	-16,73
Tenofovir	-13,32	-10,52	-9,93

* Valores da energia em kcal/mol.

Conclusões

Exceto o Tenofovir, todos os demais antivirais mostraram-se potentes para o tratamento da COVID-19, tanto na fase de pré-fusão do vírus quanto na pós-fusão, podendo desempenhar um papel importante também na prevenção do processamento pós-tradução de poliproteínas virais.

Agradecimentos

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XXI SBQT

Estudo computacional por modelagem comparativa, docking molecular e previsão ADMET de alvos moleculares frente a protease esterol 14alfa-desmetilase do *Trypanosoma cruzi*

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Palavras-Chave: Doença de Chagas, CYP51, Docking molecular.

Introdução

As doenças negligenciadas são patologias causadas por agentes infecciosos e parasitários que além de afetarem as populações pobres, contribuem para manutenção da desigualdade social.¹ A doença de Chagas é uma doença tropical causada pelo parasita *Trypanosoma cruzi*, sendo considerada negligenciada pela OMS e comumente transmitida ao homem pelo inseto vetor triatomíneo, conhecido popularmente como barbeiro.² Atualmente, a doença de Chagas afeta de 6 a 7 milhões de pessoas no mundo e calcula-se que 70 milhões de pessoas estejam em risco de contraí-la, causando cerca de 14 mil mortes por ano, em decorrência das complicações.³ Assim, surge a necessidade do planejamento e desenvolvimento de medicamentos mais eficientes para o tratamento do *T. cruzi*.

Metodologia

Para a criação do modelo, utilizou-se a sequência FASTA da protease esterol 14alfa-desmetilase (GenBank: AFW98340.1) depositada no NCBI e realizou-se o BLAST por meio da modelagem comparativa, a qual identificou a sequência de maior similaridade com 99.35% de identidade (ID: 2WUZ_A). Em seguida realizou-se o BLAST com a sequência alvo e o molde no UCSF Chimera para a obtenção e escolha do modelo de menor zDOPE. As estruturas 3D dos ligantes Benznidazol (BNZ) e Fexnidazol (FXZ) foram obtidas no PubChem com os CID 31593 e 68792, respectivamente. Enquanto que a preparação do docking molecular foi realizada com o software AutoDock Tools e os cálculos de energias de ligação (ΔG_{bind}) com o AutoDock Vina. As visualizações das interações intermoleculares dos complexos receptor-ligantes foram obtidas com o LigPlot+. As propriedades farmacocinéticas dos ligantes foram determinadas com o banco de dados PreADMET.

Resultados

Figura 1. A) Sobreposição do alvo 2WUZ_A (em azul) com o “modelo” (em bege) obtido para a protease esterol 14alfa-desmetilase (CYP51); B) Ligantes BNZ e FXZ.

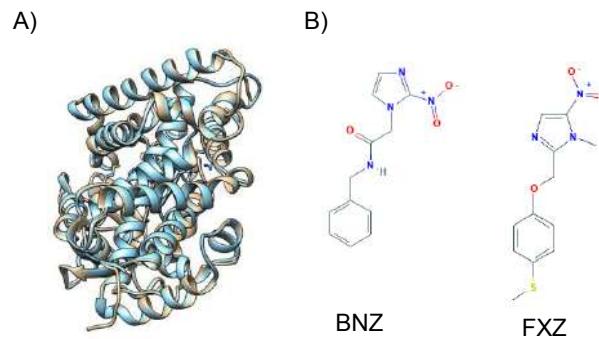


Tabela 1. Parâmetros de afinidade molecular e energias de ligação dos complexos receptor-ligantes

Comp lex	ΔG_{bind} (kcal mol ⁻¹)	Hydrogen bonds with the residues	Hydrophobic interactions with the residues
Model	-7.9	Tyr116	M106, M358, T103, V359, L356, P110, P290, A287, Hem500
-	BNZ		
Model	-7.4	Tyr116 (2)	M460, T103, P290, P110, A287, A291, Hem500
-	FXZ		

Tabela 2. Parâmetros ADME-Tox avaliados pelo PreADMET

Parameter	BNZ	FXZ
BBB	0.099	0.020
Caco2	17.299	16.254
HIA	88.483	95.112
PPB%	87.964	90.359
Carcino Mouse	Negative	Negative

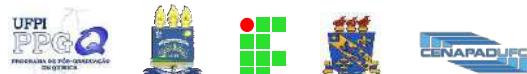
Conclusão

Conclui-se que a molécula FXZ apresenta propriedades de afinidade molecular semelhantes ao BNZ, porém com parâmetros ADMET mais promissores, os quais podem resultar em menos efeitos colaterais ao organismo dos pacientes infectados e melhor eficácia ao combate do *T. cruzi*.

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Agradecimentos



Molecular modeling for the interpretation of SERS of water contaminants: a case study for Diuron and Acephate

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Keywords: SERS, pesticides, molecular modeling.

Abstract

The indiscriminate use of chemical products in agriculture can cause numerous impacts on the environment, especially the contamination of water resources, where their detection is more difficult. In this context, new detection techniques for these compounds need to be developed.

In this context, the use of surface-enhanced Raman scattering (SERS) techniques with suspended nanoparticles (NP) have gained prominence. However, the use of SERS is particularly problematic for the detection of negatively charged compounds^[1].

In this work we use molecular modeling techniques to identify characteristics related to the local reactivities and Raman spectra of two commonly employed pesticides: acephate and diuron, as well as a promising gold NP functionalizing agent, CTAB. Our main focus is helping the analysis of SERS experiments and define sensitive approaches for the monitoring and detection of these compounds in water resources.

High-temperature molecular dynamics simulations were conducted to obtain distinct initial conformations of the compounds, which were then pre-optimized in a Hartree-Fock approach with the PM6 semi-empirical approximation^[2]. The most stable conformations were re-optimized in the framework of the density functional theory, using B3LYP hybrid functional^[3] and 6-311+G(d,p) basis set on all the atoms, via Gaussian 16 package.

The local reactivities were evaluated with the aid of the condensed-to-atoms Fukui indexes (CAFI)^[4] considering the difference of the electronic populations of anionic, neutral and cationic structures and molecular electrostatic potential (MEP). The electronic populations and vibrational Raman activities were computed using DFT/B3LYP/6-311+G(d,p) approach. Additional calculations were conducted for the systems chemisorbed with a single metal atom (Au) at the most reactive sites (identified via CAFI analysis). For these cases, the calculations were conducted in the framework of DFT/B3LYP using 6-311+G(d,p) basis set for all the light atoms and ADZP for Au^[5].

Figure 1 shows the CAFI and MEP obtained for acephate, diuron, and CTAB, red and blue colors define reactive (negative) and non-reactive (positive) sites.

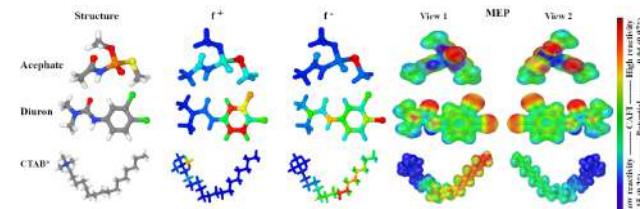


Figure 1 - CAFI and MEP representations for acephate, diuron and CTAB.

The CAFI and MEP analyses indicate the relevance of sulfur and chlorine atoms on the adsorption process of acephate and diuron, respectively. It is also interesting to note that the adsorption of positively charged portions of CTAB exposes nucleophilic centers for subsequent interaction with the pesticides.

Figure 2 shows typical Raman spectra for isolated and adsorbed compounds (with Au atoms). Note that the presence of the metal atom enhances the Raman activity at specific wavelengths, which can help the interpretation of experimental data.

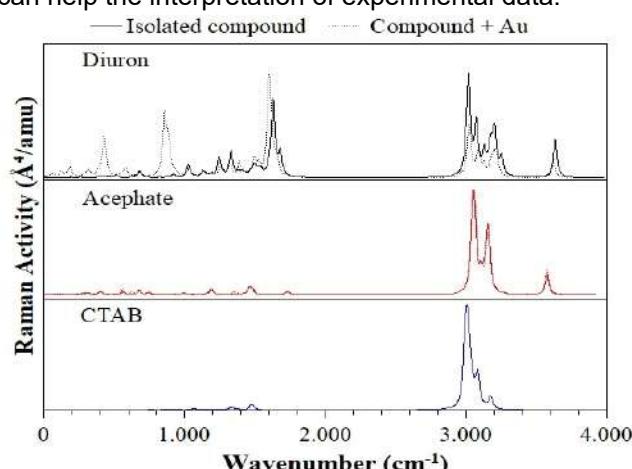


Figure 2 - Raman spectrum of acephate, diuron and CTAB.

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Electronic and structural study of $[\text{Fe}(\text{H}_2\text{O})(\text{OH}_3)]$ and O_2 adsorption in (001) and (112) chalcopyrite surface

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Keywords: chalcopyrite, DFT, adsorption

INTRODUCTION

Chalcopyrite is the largest source of copper in the world,¹ has a general formula CuFeS_2 and tetragonal structure ($I42d$) and it does not have a preferential cleavage plan. One of the copper extraction processes is called the hydrometallurgical route. One of the steps in this route is known as leaching and occurs on the mineral surface in the presence of iron sulfate and oxygen, a process with an unknown mechanism and slow kinetics.² It is of interest in this work to identify reactive sites on the (001) and (112) chalcopyrite surface, **Figure 1**, in the presence of hydrated Fe^{3+} ions and O_2 as a leaching agent.

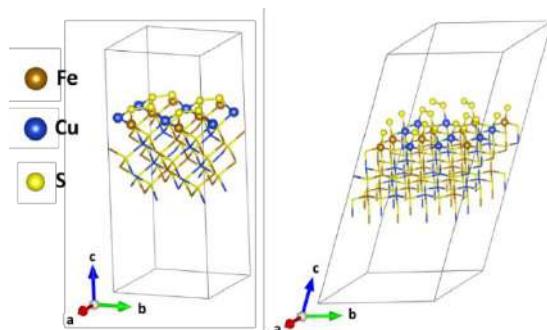


Figure 1. Optimized structures of a) (001) e b) (112) surfaces.

METHODOLOGY

The Quantum Espresso software was used for computational simulations of (001) and (112) chalcopyrite surfaces. The DFT / plane waves method was applied with PW91+U functional and ultrasoft as pseudopotential. The slab model was used for the construction of the surfaces. **Table 1** presents the parameters chosen for each surface.

Table 1. Simulation protocol.

Surface	(001)	(112)
Kinetic energy cutoff	40 Ry	30 Ry
K points – optimization	2x2x1	Gamma point
K points – post-processes	4x4x2	2x2x1
Hubbard (U) for Fe_{sup}	2 eV	2 eV

RESULTS AND DISCUSSION

One of the adsorption sites of the species $[\text{Fe}(\text{H}_2\text{O})_2(\text{OH})_3]$ in both surfaces was studied. It is observed that the adsorption on the (001) surface promotes the formation of two bonds ($\text{O}_{\text{ads}}-\text{Fe}_{\text{sur}}$ and

$\text{Fe}_{\text{ads}}-\text{S}_{\text{sur}}$), **Figure 2**. The adsorption is analogous on the (112) surface.

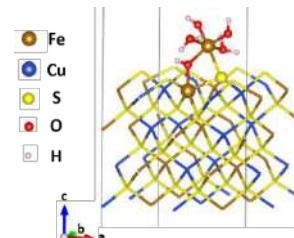


Figure 2. Optimized structure of the (001) surface with $[\text{Fe}(\text{H}_2\text{O})_2(\text{OH})_3]$ as adsorbent.

Using **Equation (1)**, it is possible to calculate the adsorption energy (ΔE_{ads}), **Table 2**, of the species on each surface.

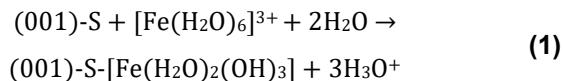


Table 2. ΔE_{ads} for the adsorption of $[\text{Fe}(\text{H}_2\text{O})_2(\text{OH})_3]$ species on the (001) and (112) surface.

Surface	$\Delta E_{\text{ads}} / \text{kcal mol}^{-1}$
(001)	-34,5
(112)	-23,4

Based on these results, it is possible conclude that adsorption is more favorable on the (001) surface than on (112). Electronic results (density of states) show electron transfer from S_{sur} to Fe_{ads} atoms.

CONCLUSION

The computation models show favorable adsorptions of the species $[\text{Fe}(\text{H}_2\text{O})_2(\text{OH})_3]$ on the chalcopyrite surfaces. The perspective is to investigate other adsorption sites for this species and O_2 adsorption. It will be possible to make a comparison between all models to understand, at the molecular level, the reactive sites involved in the first step of chalcopyrite leaching.

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NCI and ELF analysis of the second generation of BCR-ABL inhibitors: dasatinib and afatinib

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Palavras-Chave: afatinib, dasatinib, CML

Introduction

The CML disease is characterized by the severe proliferation of white blood cells with respective loss of function in its blastic stage as a result of the bad regulation from the mutant transcript of the Philadelphia chromosome, the BCR-ABL tyrosine kinase protein (PDB 1OPK) (B et al., 2003). The BCR-ABL protein can present more mutations, especially the gatekeeper mutation (T315I) and the (G363N) mutation, which disrupt the effectiveness of imatinib (PEREIRA et al 2021). In this context, some molecules were designed to replace imatinib, the first potential drug against CML, and among their lines are dasatinib (M; A, 2018). (dasatinib was rationally designed to have better interactions with the mutant protein) and afatinib (H; CF, 2018), a molecule initially applied to breast and lung cancer . The aim of this work is to study the potential of afatinib for treating imatinib-resistant CML. In this study, we investigated the Electron Localization Function (SAVIN et al., 1997) and Non-Covalent Interactions of these drugs.

Materials and Methods

The geometrical conformation of the molecules of dasatinib and afatinib were optimized through DFT (B3LYP) method using Gaussian 09 program (M. J. FRISCH et al, 2016) in a vacuum and with implicit solvent (PCM). A docking study was performed to evaluate the main interactions between the inhibitors and the target protein (RCSB PDB code 1OPK) using the AutoDock 4(GM et al., 2009) package. The NCI and ELF results were obtained through Multiwfn (LU; CHEN, 2012) software package.

Results

Figure 1 shows the isosurface results of the NCI and ELF.

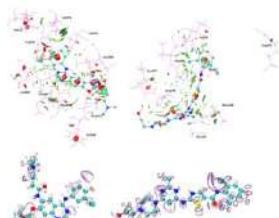


Figure 1: NCI and ELF visualizations of the ligand-protein complexes.

The electron localization function revealed that the electronic densities of the molecules are concentrated in fragments related to important attractive interactions in the drug-protein complexes, such as the central amide group and the aromatic center as well as the sulfur atom in the dasatinib

molecule. This sulfur atom performs an important role when considering the Met318 (PARK et al., 2013) residue of the target protein, which was shown to be of importance to the design of new TKIs. Also, seeing that afatinib and dasatinib have some similarities, it is possible to assume that, with some modifications, afatinib can be proposed to the treatment of CML in the same manner as dasatinib with significant results.

Conclusions

The molecules of the second generation inhibitors in this study showed some similarities and interesting interactions observing in our study using the NCI and ELF analysis. This study also presents some structures of importance when designing new drugs such as the sulfur atoms and the central amide that allow for interactions with the mutated residues.

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Hydrogen Physisorption on $(BeO)_n$, $B_2H_4(Be,Ti)$, and B_6Ti_3 Metal Clusters: A Computational Study of Energies and Atomic Partial Charges

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Key-words: hydrogen adsorption, metallic clusters, ω B97X-D

Introduction

In order to employ hydrogen as a fuel in transportation, it must be stored on board with safety and with sufficient amount. Therefore, efforts have been made to increase the H_2 storage capacity exploring the weak forces of charge-transfer and dispersion interactions (van der Waals forces) it can form with porous nanostructures. The H_2 molecule can form weak physisorption interactions with the substrate surface, or in atomic form it can chemisorbs strongly with substrate material [1]. In the former case, a low hydrogen storage is achieved with hydrogen easily desorbing, and in the later, a high storage is achieved, but desorption of H_2 is more difficult. For an efficient and reversible hydrogen storage, it is important to have hydrogen adsorbed in molecular form with adsorption energy in the range of 2.0 - 9.0 kcal/mol/ H_2 [1,2]. Recently, adsorption of H_2 on MOF (metal-organic framework) linkers [1], titanium decorated boranes [3], and $(BeO)_n$ clusters [4] have been investigated. In this present study, the capability of adsorption of H_2 are investigated on various clusters of metals as $(BeO)_n$, $B_2H_4(Be,Ti)$, and B_6Ti_3 . Our old common sense of classical chemists still insists on trying visualizes individual atoms in molecules. Thus, in this study the accuracy of some popular methods are explored in predicting the atomic charges in difficult cases involving different kinds of chemical bonds and weak H_2 intermolecular interactions

Methods

The equilibrium structures of isolated clusters and adsorbed by H_2 molecules were computed with the ω B97X-D method and employing the 6-31+G(2d,2p) basis set, which was validated in previous studies of H_2 adsorption beryllium clusters [4]. The calculated energetic quantities are the electronic energies, enthalpy of reaction at 0 K, enthalpy at 298 K, and the Gibbs free energy. Various methods of partial charges calculations were explored as the Mulliken, Natural Population Analysis (NPA), CHELPG, and Hirshfeld [5]. The GAUSSIAN code was employed in the calculations of equilibrium geometries, harmonic frequencies, and thermodynamics quantities.

Results and discussion

The studied species are formed by different types of bonds and in the case of boranes their electronic structures are versatile since they can easily form covalent and intermolecular dispersion bonds.

Calculations show that the titanium - borane clusters have reasonable energy stabilization with values of enthalpy at 298 K in the temperature range adequate for applications of hydrogen storage, i.e., 9.0 to 13.0 kcal/mol (Table). Calculations of the cluster $B_6Ti_3.10H_2$ give best capacity of hydrogen adsorption, if are considered the energy adsorption ($\Delta G_{298} = -5.1$ kcal/mol) and the number of H_2 molecules adsorbed, giving a gravimetric uptake capacity equal to 9.8 wt% that exceeds, for example, the target set by US Department of Energy for Vehicular Application of 2025 [2]. This favorable result occurs in reason of the high ability of clusters of boranes and titanium atoms in forming covalent and dispersion interactions. Calculations with the Hirshfeld atomic density charges give more reliable results in cases of chemical bonding between the atoms of boron and titanium which have almost equal electronegativity. For the borane derivative clusters, was found a quantitative correlation between difference of atomic charges of isolated and the adsorbed H_2 molecules with the adsorption energies (E_a).

Table Values (in kcal/mol) of adsorption energies (E_a) E_e , ΔH_0 , ΔH_{298} , and ΔG_{298} .

Species	E_e	ΔH_0	ΔH_{298}	ΔG_{298}
$(BeO)_2.12H_2$	-3.0	-0.6	0.0	0.0
$(BeO)_4.8H_2$	-2.0	-1.3	-0.7	5.1
$B_2H_4Be.H_2$	-12.4	-8.2	-9.6	-1.6
$B_2H_4Ti.4H_2$	-15.6	-11.7	-13.6	-4.9
$B_6Ti_3.10H_2$	-15.5	-11.9	-13.3	-5.1

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Busca e análise de mínimo global de dicátons aromáticos

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Palavras-Chave: Aromáticos, DFT, AUTOMATON

INTRODUÇÃO

A detecção de espécies duplamente ionizadas, assim como a determinação da geometria de mínimo global do benzeno¹ influenciou estudos do mecanismo de fragmentação e do mapeamento das possíveis estruturas de intermediários e produtos.

Para compreender esses mecanismos, a fragmentação de espécies aromáticas por impacto de elétrons foi realizada utilizando um espectrômetro de massas de alta resolução por tempo de voo (reflectron). As moléculas estudadas foram benzeno, tolueno, anilina, anisol, clorobenzeno e cicloexano. O cicloexano foi incluído para obtenção de um padrão de fragmentação de um sistema não aromático. No espectro de massas foram verificados picos com razão m/z fracionárias indicando resistência à fragmentação de dicátons contendo seis átomos de carbono.

Além disso, os picos m/z 37,5, 38,5 e 39,5 estão presentes em todos os espectros dos compostos estudados exceto para o cicloexano. Dessa forma, as estruturas de fórmula C₆H₅²⁺, C₆H₄²⁺ e C₆H₃²⁺ são fragmentos oriundos de moléculas aromáticas com anéis de seis membros.

O objetivo deste trabalho é analisar as estruturas de mínimo obtidas através do programa de algoritmo genético AUTOMATON² para cada fragmento duplamente ionizado observado experimentalmente.

MÉTODO

Cálculos de busca sistemática de mínimo global foram realizados para a molécula C₆H₆²⁺ utilizando o método de algoritmo genético implementado no programa AUTOMATON acoplado ao programa Gaussian para validar o protocolo³. Os cálculos foram realizados em nível DFT com o funcional PBE0 nas bases 6-31G(d), 3-21G e SDDAll, partindo de 5N e 7N indivíduos iniciais, onde N é o número de átomos do sistema. O uso de bases de qualidade double-zeta para a varredura de estruturas é justificado devido ao elevado números de estruturas iniciais geradas e o funcional PBE0 é adequado para o estudo de dicátons aromáticos⁴.

Repetiu-se o processo para os fragmentos C₆H₅²⁺, C₆H₄²⁺ e C₆H₃²⁺ nos melhores padrões de validação e reotimizou-se as cinco estruturas de mínimo na base def2-TZVPP com cálculo de frequência e correção de energia ZPE.

RESULTADOS

Os melhores resultados foram obtidos na base 6-31G(d) partindo de 7N indivíduos, onde se

encontrou pirâmide de base pentagonal como mínimo entre outras já reportadas na literatura.



Figura 1: Estruturas do C₆H₆²⁺ (PBE0/6-31G(d), 7N) Após a reotimização, PBE0/def2-TZVPP, encontrou-se, para as espécies C₆H₅²⁺, C₆H₄²⁺ e C₆H₃²⁺, as cinco estruturas mais estáveis em ordem crescente de energia.

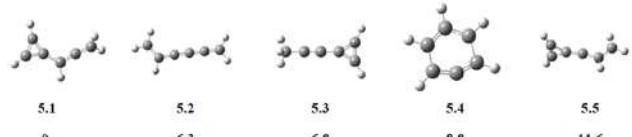


Figura 2: Estruturas do C₆H₅²⁺

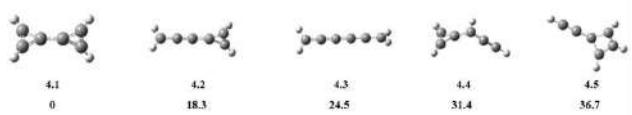


Figura 3: Estruturas do C₆H₄²⁺

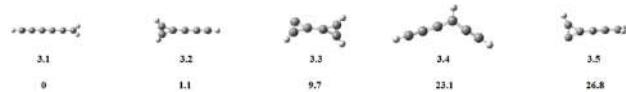


Figura 4: Estruturas do C₆H₃²⁺

CONCLUSÕES

Por mais que os dicátons aromáticos representem um desafio devido a concentração de cargas positivas, o programa AUTOMATON conseguiu encontrar a estrutura desejada para o benzeno, porém com padrões iniciais diferentes do indicado no artigo original. Assim, dependendo da molécula estudada, necessita-se encontrar os parâmetros mínimos para tal.

Das quinze estruturas reotimizadas dos fragmentos, apenas quatro contêm a cadeia totalmente linear. Mesmo 3.1 possui energia relativa muito próxima a 3.2, mostrando a persistência do ciclopripil nestas espécies, como também outras partes cíclicas, presente em 5.4 e 4.5.

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Assessing staurosporine analogs conformational ensemble

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Palavras-Chave: *indolocarbazoles, molecular dynamics, conformation*.

Introduction

Indolocarbazoles are glycosylated natural products presenting wide chemical diversity and broad spectrum of biological activity, notably antitumor, and antimicrobial (Nettleton *et al*, 1985; Nakano *et al*, 2009). However staurosporine and analogs compounds (STA-analogs) has been pointed as potent kinases inhibitors (Omura *et al*, 1995, Komander *et al*, 2003), its non-specificity also leads to high rates of toxicity, limiting its application in clinics (Gani *et al*, 2010). Although STA-analogs complexed with target proteins are already described, supporting structure-based optimization of its bioactive properties, the conformational features of its flexible substituents, such as the glycan moieties, are still partially inaccessible to state of the art structural biology methods. As a complement to these methods, molecular mechanics based calculations may offer a unique set of tools to assess the conformational ensemble of STA-analogs allowing new insights to refine its structure activity relationships (SAR) in biological solutions.

Methods

In order to assess the conformational features of STA-analogs in a pre-complexation state, molecular dynamics (MD) simulations were performed through GROMOS force field. Quantum calculations at the MP2 level were implemented by Gaussian and supplied the dihedral potentials and the partial atomic charges, whose parameters were fitted to better reproduce on classical mechanics the rotational bonds profile (Rusu *et al*, 2020) and the chromophore vector dipole moment of molecules (Arantes *et al*, 2020). Each compound was placed in a dodecahedron box with SPC/E water molecules and simulations were carried out using GROMACS package for 1 μ s. Through the PLUMED package it was possible to expand the glycan moieties puckering sampling.

Results

The new force field parameters enable to perform simulations of STA-analogs presenting different substituents and glycan moieties. Some structural modification patterns showed to be involved on solute-water H-bond, with diverse lifetimes and dihedral freedom degrees. The opposite orientations of the hydroxyl group at the stereoisomers UCN-01 and UCN-02 interact with the water bulk forming different hydration water networks and affecting the rotational degrees of freedom of the methylamine group attached to the sugar (Jong *et al*, 2018). The

puckering free energy landscape of pyranoses with different substitution complexity (including bicycle and tricycle structures) attached to staurosporine (Link *et al*, 1996), ZHD-0501 and N-acetylated staurosporine presented multiple energy minimums from biased MD simulations. Together, the detailing of the flexibility of these compounds expand the perception of possible STA-analogs conformers in biological solution when compared to classical structural biology methods.

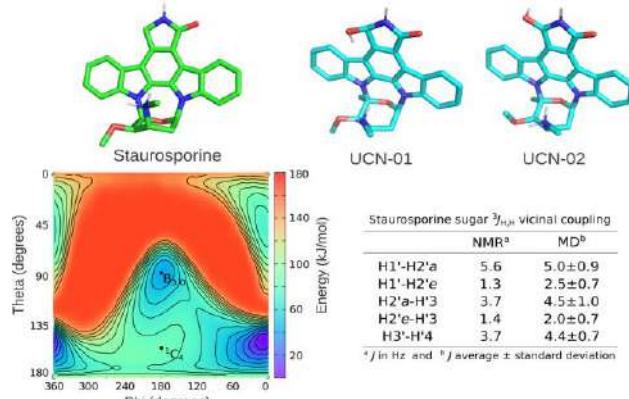


Figure 1: Staurosporine (green) and analogs (cyan). Sugar puckering free energy landscape showing two conformers B_{3,O} and C₄. Table comparing ³J_{H,H} vicinal coupling constant from NMR and its prediction from MD.

Conclusions

Differential substitution changes regarding H-bonds lifetimes with the solvent could affect the STA-analogs complexation free energy due to the desolvation energetic costs. The broad perception of the STA-analogs flexibility in solution represents a potential factor to be exploited aiming to improve the specificity of these ligands and to expand the therapeutic use of these compounds class.

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Electronic effect of the support on the physicochemical properties of catalyst clusters models of MnO.Mn₂O₃/S; (S=Al₂O₃, SiO₂ e TiO₂)

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Palavras-Chave: Catalyst Molecular Models. Physicochemical properties. CASPT2.

Introduction

The catalytic property of materials can be improved or attenuated through the electronic interaction between the support and the active phase, since depending on the chemical composition of the support, there may or may not be electron transfer between the active phase and the support. Thus, in the present work, the physicochemical properties of the catalyst models built by combining the active phase (MnO.Mn₂O₃) with the supports (Al₂O₃, SiO₂, and TiO₂) were studied by ab initio methods.

Methodology

The geometry optimization was performed using the methodology DFT//M06/Def2-SVP. While the electronic ground state and the electronic excited states were characterized through calculations *single-point* through the CASPT2//DFT/M06/Def2-SVP methodology. The stability of metal oxide clusters was studied using the stability ranking function (ε^3)^[1], and the reactivity was evaluated by the net electrophilicity index ($\Delta\omega^\pm$).

Results

As can be seen in Figure 1, depending on the support, the active phase presents different types of fitting: replacement of an atom of the support, Al₂O₃, or fit into the top position of the support (connected by 3 or 2 oxygen atoms, TiO₂ e SiO₂, respectively).

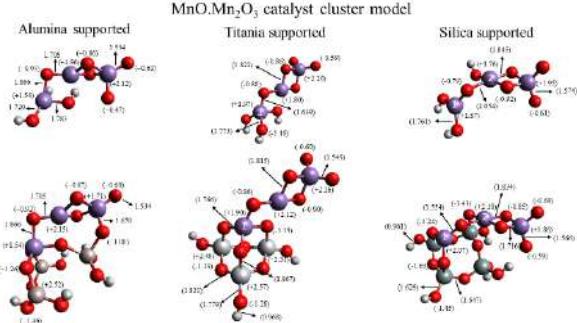


Figura 1. Optimized geometries of MnO.Mn₂O₃ catalysts supported on alumina, titania, and silica obtained by the DFT//M06/Def2SVP methodology.

In addition to conformational changes in the active site, changes in the partial charges of manganese atoms generated by the exchange of support are also observed. As expected, there is a greater charge transfer between the manganese-support, demarcated as 1 and 2, in the SiO₂ agglomerate than in the TiO₂, in the order of +0.27 and -0.07, respectively, due to the higher

electronegativity of silicon (1.9) in relation to manganese (1.55) and titanium (1.54). This lack of charge on the active site caused by the silica support can generate some effects on the molecular properties of the catalyst, such as an increase in both the ionization potential and the electronic affinity, given the lack of electrons, which, consequently, intensifies the reactivity of the catalyst.

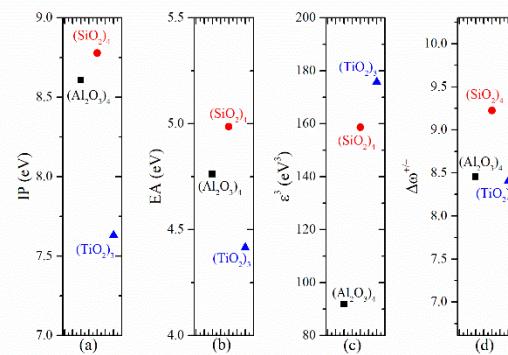


Figura 2. Ionization potential (a), electronic affinity (b), ε^3 (c) e $\Delta\omega^\pm$ (d) of the catalyst molecular models of MnO.Mn₂O₃ supported on alumina (black), titania (blue) e sílica (red) obtained by the DFT//M06/Def2SVP methodology.

As expected, both the ionization potential and the electron affinity are higher in MnO.Mn₂O₃/(SiO₂)₄ than in MnO.Mn₂O₃/(TiO₂)₃, due to the greater electronegativity difference between silicon and manganese, which, consequently, leads to greater reactivity ($\Delta\omega^\pm$). Combining the stability and reactivity information, it can be seen that the MnO.Mn₂O₃/(SiO₂)₄ cluster is a possible catalyst candidate for presenting a balance between reactivity and stability, being reactive to provoke a reaction and stable enough to be regenerated at the end of the catalytic cycle.

Conclusion

The use of tools capable of scanning the desired physicochemical properties is of great interest in the design of new materials, as it allows the identification of possible candidates for new devices, such as MnO.Mn₂O₃/(SiO₂)₄ for hydrogen peroxide decomposition.

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Avaliação de experimental e DFT dos deslocamentos químicos de RMN ¹H de um novo derivado da Ftaloilglicina

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Palavras-Chave: Ftaloilglicina, RMN, DFT.

INTRODUÇÃO

As ftalimidas são definidas como imidas cíclicas e apresentam uma diversidade atividades biológicas como anticâncer¹, antimalarial² e antimicrobiana³. Nesse trabalho, um novo derivado da Ftaloilglicina foi sintetizado e caracterizado por RMN ¹H. Além disso, foram avaliados quatro funcionais DFT na predição dos deslocamentos químicos ¹H do composto.

METODOLOGIA

O Ftaloilglicinato de 2-(4-metilfenil)-2-oxoetila foi sintetizado a partir da reação de substituição nucleofílica S_N2 entre o ftaloilglicinato de potássio com a 2-bromo-4'metilacetofenona a 100°C usando o solvente DMF, de acordo com o esquema da Figura 1.

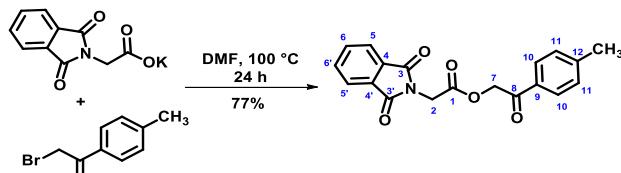


Figura 1: Síntese do composto Ftaloilglicinato de 2-(4-metilfenil)-2-oxoetila.

Os sinais teóricos de RMN de ¹H do composto foram obtidos a partir de cálculos DFT (B3LYP, ωB97XD, CAM-B3LYP e BHandHLYP) em combinação com modelo de solvatação CPCM para simular o efeito do solvente clorofórmio. Foi aplicada a base 6-31+G(d) para obter a estrutura de mínimo e o modelo Orbital Atômico de Calibre Independente (GIAO). Todos os cálculos foram realizados utilizando o software Gaussian09 D01².

RESULTADOS

O composto foi caracterizado pela técnica de espectroscopia de RMN de ¹H em clorofórmio deuterado. Na Tabela 1 são comparados os valores

de deslocamentos químicos ¹H calculados e experimentais do composto.

Tabela 1. Deslocamentos químicos de RMN ¹H calculados e experimentais (ppm).

δ_H	B3LYP	ω B97XD	CAM-B3LYP	BHandHLYP	Experimental
2	3,79	3,72	3,78	3,74	4,65
5	7,40	7,91	7,55	7,67	7,74
6	7,38	7,78	7,49	7,57	7,86
7	4,54	4,49	4,57	4,50	5,41
10	7,56	7,62	7,69	7,80	7,78
11	7,00	7,15	7,09	7,15	7,26
CH ₃	2,05	2,36	2,08	2,10	2,40
DMA	0,49	0,35	0,41	0,38	
R ²	0,9866	0,9673	0,984	0,9791	

DMA = Desvio Médio Absoluto; R² = Coeficiente de Correlação Linear

CONCLUSÃO

Na comparação entre os espectros teóricos e experimentais, os funcionais ω B97XD e Bhandhlyp forneceram os melhores resultados dentre os funcionais estudados. Desse modo, essa metodologia configura-se como promissora para estudos subsequentes de derivados da Ftaloilglicina.

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Non-Adiabatic Gas-Phase Formation of HPSi, the Isovalent Counterpart of HNC

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Keywords: Phosphinidenesilylene, Density Functional Theory, Intersystem Crossing.

Introduction

Since the isolation of hydrogen cyanide (HCN, **1**) from Prussian Blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) by the Swedish chemist Carl Wilhelm Scheele in 1782,^[1] the structural isomer (HNC, **2**) and the isovalent homologues (HSiN, **3**; HNSi, **4**; HCP, **5**; HPC, **6**; HSiP, **7**; HPSi, **8**) have intrigued the scientific community from the fundamental aspects of electronic structure and chemical bonding. Within the astrochemistry domain, interstellar detection of **1**, **2** and **5** via rotational transitions was already reported.^[2-4] The other homologues, however, have eluded any astronomical detection to date.

Herein we provide a glance into the unknown chemistry of phosphinidenesilylene (HPSi, **8**). Our investigation with electronic structure calculations, in collaboration with crossed molecular beam experiments, provides a unique look into the exotic reaction mechanisms and non-adiabatic reaction dynamics through which highly reactive P-Si molecules like **8** are prepared as a result of a single collision between open-shell atomic silicon and the prototype closed-shell P-bearing molecule (phosphine).^[5]

Methodology

DFT calculations were performed with the M06-2X exchange and correlation functional and cc-pV(T+d)Z basis set. Vibrational analyses were carried out for all stationary points found in order to confirm whether they corresponded to energy minima or transition states (TSs). Intrinsic reaction coordinate (IRC) calculations starting from each TS were performed to ensure the correct connection paths. The reported energies of all structures are zero-point energy (ZPE) corrected and no symmetry restrictions were imposed in any calculation. To further improve the accuracy of our results, we have also performed single point energy calculations at the CCSD(T)-F12/aug-cc-pV(T+d)Z level in all obtained geometries.

Results and Conclusions

Our calculations predict a barrierless route to HPSi ($X^1\text{A}'$) formation from gas-phase reaction of ground-state atomic silicon ($\text{Si}; ^3\text{P}$) with phosphine (PH_3 ; $X^1\text{A}_1$). The unraveling of non-adiabatic reaction dynamics necessitates the exploration of the triplet and singlet SiPH_3 potential energy surfaces. Our computations^[5] located 7 triplet and 3 singlet

intermediates, 21 TSs and 2 minima on the singlet-triplet seam of crossings.

The chemical dynamics is initiated on the triplet surface via addition of a Si atom to the non-bonding electron pair of PH_3 , followed by surface hopping to the singlet manifold (shown in Fig.1), accompanied by isomerization via atomic hydrogen shift and decomposition to phosphinidenesilylene (HPSi, **p1**; $X^1\text{A}'$; $\Delta_r\text{E} = -159 \text{ kJ mol}^{-1}$) along with molecular hydrogen.

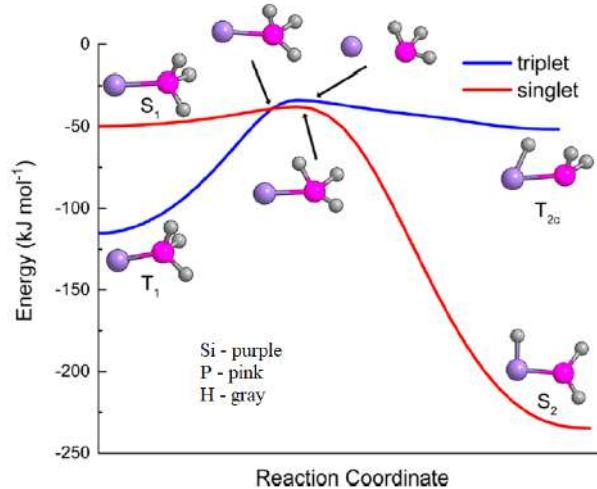


Fig.1 – IRC results showing the singlet-triplet crossing. Energies are relative to reactants.

Statistical calculations predict that silylidynephosphine (HSiP, **p2**; $X^1\Sigma^+$; $\Delta_r\text{E} = -114 \text{ kJ mol}^{-1}$) is also formed, but with lower yields. These results agree well with the gas-phase synthesis carried out via crossed molecular beams reaction under single-collision conditions. Our studies suggest that the most stable products (**p1** and **p2**) obtained are potential candidates for searches in circumstellar envelopes and towards star-forming regions where phosphine has been detected.^[6]

Acknowledgements

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Estudo da Decomposição Térmica do Sistema H₂O₂/H₂O e Suas Aplicações na Indústria Aeroespacial.

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Palavras-Chave:Modelo cinético, decomposição térmica, DFT

Introdução

O peróxido de hidrogênio foi muito utilizado no passado em sistemas a monopropelente ou como oxidante em sistemas a bipropelente. No entanto, foi substituído pela hidrazina e seus derivados. Nos dias de hoje, a busca por propelentes verdes trouxe de volta a possibilidade de uso do H₂O₂ na indústria aeroespacial. Pouca pesquisa básica sobre a decomposição térmica e detonação de soluções concentradas de H₂O₂ para uso em foguetes é encontrada na literatura. Por estas razões, a cinética da degradação térmica de misturas H₂O₂/H₂O, na presença e ausência de catalisadores, foi revisitada e propriedades de propelentes foram calculados.

Metodologia

A primeira parte do estudo foi a modelagem da decomposição térmica da mistura H₂O₂/H₂O e a simulação de três modelos cinéticos distintos. Quando possível, desvios do comportamento ideal foram corrigidos pelo uso da equação de estado de Redlich-Kwong. As simulações foram realizadas nos códigos Cantera¹ e Detonation Toolbox².

Devido à falta de parâmetros cinéticos para reação na superfície no catalisador, o mecanismo de reação para decomposição do H₂O₂ na presença de Fe, Fe⁺ e Fe²⁺ tem sido investigado. Este estudo utiliza os métodos M06-2x e CCSD(T), com base cc-pvtz para descrição dos átomos de hidrogênio e oxigênio e o pseudo-potencial de Los Alamos para descrição do átomo de ferro. Todos os cálculos foram realizados no Gaussian 16³.

Resultados e Discussão:

Como um dos principais objetivos é compreender o mecanismo de reação que levam ao início da decomposição da mistura H₂O₂/H₂O, a análise de fluxo e velocidade foram realizadas(Figura 1). Segundo a análise de velocidade, inicialmente H₂O₂ se decompõe em radicais OH que é um dos principais propagadores da cadeia de decomposição.

Cálculos de propriedades como temperatura de decomposição adiabática e impulso específico mostram como o catalisador empregado absorve parte do calor liberado na decomposição do H₂O₂, diminuindo o impulso teórico. Devido à importância

do catalisador, um estudo das reações de decomposição de H₂O₂ na presença de átomos de ferro está sendo conduzido.

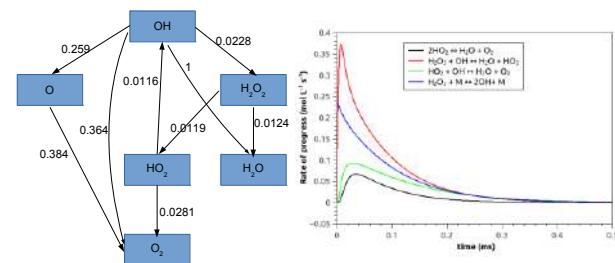


Figura 1: Análise de fluxo e velocidade do mecanismo de decomposição da mistura H₂O₂/H₂O.

A Figura 2 apresenta resultados para formação do complexo Fe(0)–H₂O₂. Em uma primeira etapa, o peróxido interage com ferro formando um complexo. Posteriormente, o sistema passa por um TS que levará a quebra da ligação peroxídica.

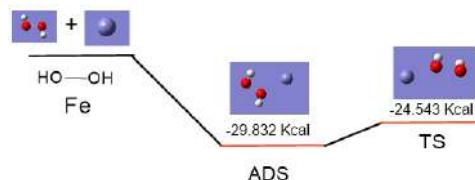


Figura 2: Interação do H₂O₂ com átomos de Fe. Estruturas otimizadas com funcional M06-2x.

Conclusões

Os modelos cinéticos propostos se mostraram confiáveis para simulação da decomposição térmica da mistura H₂O₂/H₂O na presença e ausência de catalisadores. Mas ainda são necessários dados cinéticos e termodinâmicos para realização de simulações numéricas mais complexas.

Agradecimentos

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Predição de concentração de soluções com IA explicável

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Palavras-chave: Visão computacional, desenvolvimento de algoritmos, reconstrução espectral.

RESUMO

Neste trabalho, foi desenvolvido um algoritmo de aprendizado de máquina para realizar a previsão de concentrações de corantes. O algoritmo de regressão apresentou um coeficiente de determinação de 0,93 em um conjunto de validação, indicando potencial de generalização.

INTRODUÇÃO

A técnica *Spectral Reconstruction* (SR) consiste em recuperar informações de um espectro eletromagnético a partir de um espectro com menos canais, como por exemplo uma imagem no formato RGB, onde apenas 3 canais são contemplados: vermelho, verde e azul. Partindo do princípio que é possível reconstruir o espectro de uma imagem, alguns trabalhos buscaram utilizar técnicas de Visão Computacional para determinar a concentração de substâncias a partir de imagens, como por exemplo, a concentração de clorofitas a e b em folhas [1] e parâmetros de qualidade de água [2].

Neste trabalho, o objetivo foi desenvolver um algoritmo de visão computacional e aprendizado de máquina, constituindo um método de inteligência artificial explicável (*eXplainable Artificial Intelligence* - XAI), para determinar a concentração de corantes.

METODOLOGIA

Soluções contendo um corante comercial e água foram preparadas nas seguintes concentrações: 100 g/L, 16 g/L e 2,56 g/L. Também preparamos uma amostra de água para servir como *baseline* (0 g/L). As amostras foram posicionadas sobre um fundo branco com uma micropipeta (Figura 1).



Figura 1: Exemplos de amostras com as concentrações analisadas neste trabalho.

Todas as imagens foram obtidas com uma câmera de 16 megapixels e foram redimensionadas para 28 pixels de largura por 28 pixels de altura. O total de amostras analisadas neste trabalho foi 738, divididos aleatoriamente de forma que 587 foram utilizadas para treinar o modelo e as demais 196 foram utilizadas para realizar a validação. O vetor de características foi definido da curva de densidade óptica nos três canais da imagem. O modelo de

regressão utilizado foi o *Random Forest Regressor*. desenvolvido na linguagem de programação *Python*.

RESULTADOS

Os resultados obtidos com os conjuntos de treino e validação estão apresentados na Figura 2.

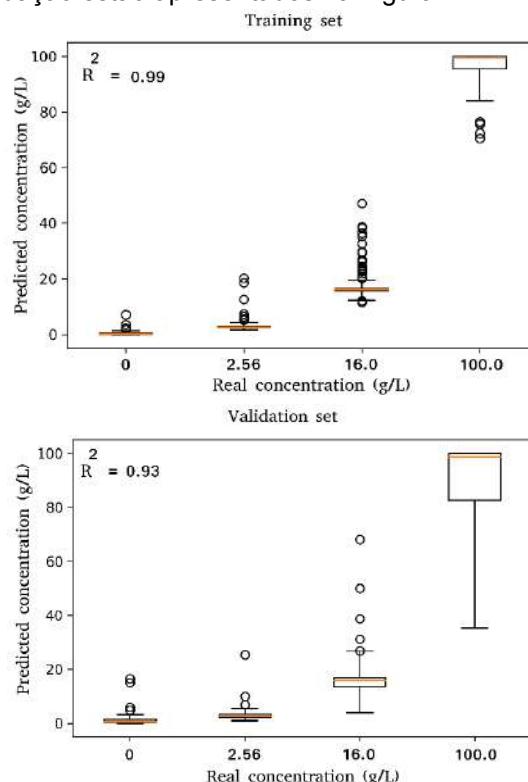


Figura 2: Resultados obtidos do modelo de regressão desenvolvido.

CONCLUSÃO

Neste trabalho inicial, o algoritmo de XAI apresentou alta performance na predição de concentração de soluções.

AGRADECIMENTOS

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Unveiling the hafnium speciation in acid aqueous solution

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Palavras-Chave: DFT, Hafnium, Paper Spray Ionization.

Introduction

The separation processes of tetravalent ions such as Zr(IV) and Hf(IV) have offered a paradigm shift in the production of strategic elements. Therefore, an understanding of speciation and the fundamental coordination chemistry of zirconium and hafnium is essential. The present study aims to elucidate the species of Hf(IV) present in an aqueous acidic solution. We combine paper spray ionization mass spectrometry (PSI-MS) and Density Functional Theory (DFT) calculations. Hence, PSI-MS transfers ions from the condensed to the gas phase, whereas DFT calculations provide detailed information regarding their stability and structure. Because the separation/extraction processes occur in a nitric medium, the proposed acidic medium used herein contains high contents of nitrate (NO_3^-) and fluoride (F^-) to simulate the conditions of alternatives extraction routes.

Results and Discussion

The results roughly reflect the species distribution in the condensed phase, and the correct alignment between the theoretical and experimental isotopic distributions of Hf(IV) (^{176}Hf (5.21%); ^{177}Hf (18.6%); ^{178}Hf (27.3%); ^{179}Hf (13.63%) and ^{180}Hf (35.1%)), can provide additional evidence of the species formation. The mass spectrum of the aqueous acidic solution of Hf(IV) is shown in Figure 1.

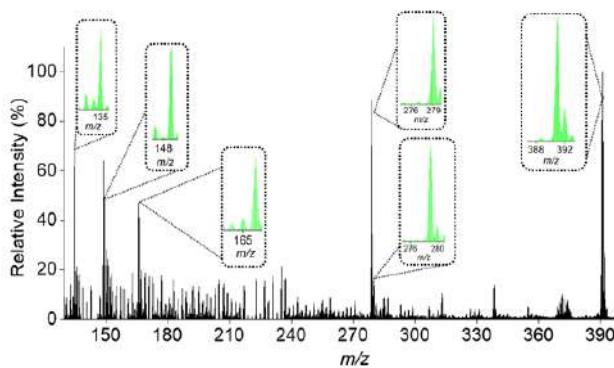


Figure 1. PSI mass spectra of Hf(IV) (10^{-4} mol L $^{-1}$) in HNO_3 (5%) and HF (0.5%) at pH 3, in positive mode. The highlights are the isotopic distributions of species.

DFT calculations were performed based on the Hf(IV) species identified by PSI-MS (Figure 2).

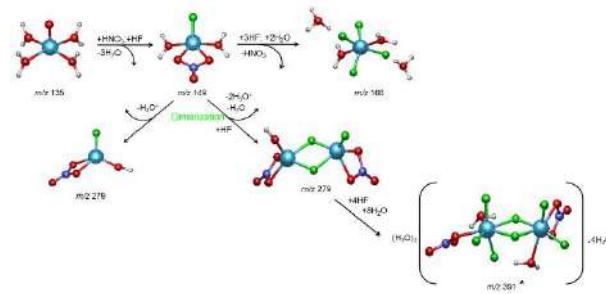


Figure 2. Positive Hf(IV) species were calculated by PBE/def2-TZVP. Reaction path proposed from m/z in positive mode. (* The H_3O^+ and H_2O present in the outer coordination sphere have been removed and calculated separately. The estimates of ΔG includes the outer sphere molecules).

The ΔG values for the $[\text{HfFOHNO}_3]^+$ (9.6 kcal.mol $^{-1}$) species is endergonic and, hence, is not thermodynamically favorable compared to the $[\text{HfO}(\text{H}_2\text{O})_4]^{2+}$. The tetrahedral and trigonal bipyramidal geometries, for $[\text{HfFOHNO}_3]^+$ and $[\text{HfNO}_3(\text{H}_2\text{O})_2]^{2+}$, respectively, may be indicative of intermediates to the formation of Hf(IV) species with higher coordination numbers (7 and 8). Also, these two monomers are precursors to the formation of the $[\text{Hf}_2\text{F}_3\text{OH}(\text{NO}_3)_2]^{2+}$ dimer with pentacoordinate metal centers. The formation of the dimeric species $(\text{H}_3\text{O})_3[\text{Hf}_2\text{F}_7(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}^{2+}$, from the oxophilic monomer $[\text{HfO}(\text{H}_2\text{O})_4]^{2+}$ provided high thermodynamic stability, c.a. -95 kcal.mol $^{-1}$. The formation of the dimer coordinated to seven F $^-$ ions shows the high affinity of Hf(IV) to fluoride.

Conclusion

A variety of species with different structures of hafnium were detected by PSI-MS. Although the species identification might seem random, the combination of well-defined isotopic envelopes and DFT calculations confirm the affinity of hafnium to different anions. DFT calculations suggest the formation of intermediates or precursors for dimerization reactions, and species with a larger ratio of metal:fluorine is favored, probably due to a synergic influence.

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Prediction of surface properties and reactivity of $\alpha\text{-MnMoO}_4$ materials: a DFT study

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Palavras-Chave: Photocatalysis; Antiviral and bactericide, Magnetism.

To maintain the fast technological advance experienced in our modern society, new materials that attend to some specific features are mandatory. Thus, the interest in novel environment-friendly materials with exciting properties and low fabrication costs increases drastically. Among the limited number of candidates that meeting such conditions stands out the manganese molybdate (MnMoO_4), which is a semiconductor material extensively employed as a supercapacitor in the development of all kinds of portable devices, electric/hybrid vehicles components, industrial power, instant switches, backup power sources, varied start engines, energy management, and others. Although this material is widely used for such purposes, the technological potential of Manganese Molybdate is not entirely known.

This manuscript reports a careful DFT/B3LYP investigation of surface properties and morphologies for the MnMoO_4 in the C2/m space group presenting an in-depth DFT investigation of electronic, optical, structural, magnetic, and photocatalytic properties of surfaces. The structural, magnetic, electronic, optical, and photocatalytic properties of the main surfaces were investigated. The surface and morphological features of the $\alpha\text{-MnMoO}_4$ material in the C2/m space group were calculated using a DFT/B3LYP approach. From the optimized bulk structure, the surface models were cut out along different crystalline directions parallel to specific hkl planes selected according to the prominent peaks observed on XRD results. Thus, the low-index (220), (-112), (021), (112), (-222), (201), and (-202) surfaces were evaluated by stoichiometric models obtained from different slab stacking and compared in terms of surface energy. The evaluated crystalline directions are polar surfaces since they present significant macroscopic dipole moment (μ_Z).

The results indicates that the stability of $\alpha\text{-MnMoO}_4$ surfaces decreases in the order (220) > (-222) > (112) > (-202) > (-112) > (021) > (201). The different surface energies can be justified by the density of defects (vacancies) in the surface, surface symmetric or non-symmetric terminations and chemical composition of surface termination. The investigation of magnetic properties indicates an antiferromagnetic ground state for (220), (-112), (021), and (201) surfaces and a ferrimagnetic ground state for (112) and (-202) surfaces. A high number of vacancies around the Mn and Mo sites creates a spin population on Mo sites for both terminations on (-112)

surfaces and O atoms on TD terminations of (-202) surfaces. Thus, local magnetic moments are observed in these non-magnetic sites. Meanwhile, the evaluation of the density of states indicates that, for all surfaces, O atoms present a relevant contribution to the VB and CB, Mn species contribute significantly to the formation of VB and CB. In contrast, the Mo species contributes majorly on the top of VB and overall of CB. The band structure also indicates the existence of flat bands for (021), (112), and (-202) surfaces, being this behavior raised from O vacancies neighboring the Mn and Mo sites in the surface. Further, the stability of charge carriers, allied to suitable band gaps values, indicates a high photocatalytic potential for (-202), (-112), and (021) surfaces.

The valence and conduction band edge potential vs. NHE electrode indicates that bulk and surfaces of MnMoO_4 can oxidize H_2O molecules to produce O_2 or oxidize pollutants. The results also suggest that the bulk and (220) and (021) surfaces can reduce H^+ to H_2 . In this context, all investigated $\alpha\text{-MnMoO}_4$ surfaces present a possible antiviral and bactericidal potential since they can produce at least one type of reactive oxygen species (ROS). The (220), (-222), and (021) surfaces stand out as the most promising alternatives due to their ability to produce five different ROS. The reactivity of surfaces was confirmed by kinetic and thermodynamic evaluation of water reactions in surface sites.

Finally, a large set of available morphologies for $\alpha\text{-MnMoO}_4$ were predicted. A high versatility was found since one crystal shape is suitable for at least two different technological purposes such as electronic, optical, magnetic, photocatalytic, or water splitting. The prediction of a large set of crystal shapes to solid-state materials is critical to materials development and provides a valuable strategy to control its properties through morphology adaptation. Thus, this study is strongly indicated to guide experimental scientists focused on novel or improved applications of $\alpha\text{-MnMoO}_4$ predicting the potential applications for each available morphology.

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Simulação computacional da adsorção de ânions na interface micela-solução

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Palavras-Chave: Micelas zwitteriônicas, simulação computacional, dinâmica molecular.

INTRODUÇÃO

Micelas zwitteriônicas não apresentam carga formal, no entanto, apresentam propriedades características das micelas carregadas, como a interação (seletiva) com íons em solução. A adsorção de íons na interface com a micela/solução é responsável por diversas aplicações, como a catálise de reações químicas, estabilização e síntese de nanopartículas. Logo, esta adsorção vem sendo amplamente estudada em eletroquímica, química de superfície e coloides, em estudos teóricos e experimentais. De modo geral, a adsorção de ânions segue a série direta de Hofmeister¹, em que grandes ânions (baixa carga e hidratação, PF₆⁻ e ClO₄⁻) interagem mais fortemente que ânions pequenos (fortemente hidratados, OH⁻ e F⁻). No entanto, a carga e a hidrofilicidade da superfície da micela, além de parâmetros como temperatura, concentração de sal e pH, alteram a forma com que os íons adsorcem^{2,3}. Diante disso, nosso objetivo foi investigar, com simulação computacional por dinâmica molecular, os efeitos da adsorção de diferentes ânions na interface micela-solução de duas micelas: hexadecilfosfetoanolamina (HPE) e hexadecilfosforilcolina (HPC), que apresentam diferentes grupos polares e, consequentemente, diferentes graus de hidrofilicidade, para comparação.

METODOLOGIA

Foram realizadas simulações de dinâmica molecular (MD) de micelas zwitteriônicas (HPC e HPE), com e sem adição de sais de sódio (NaF, NaCl, NaBr e NaClO₄) em diferentes forças iônicas (0,015 e 0,15 mol/L), utilizando o campo de força LIPID14/GAFF⁴ implementado no pacote AMBER 16⁵. Inicialmente foi realizada uma etapa de minimização (2000 ciclos) e uma etapa de equilíbrio NVT de 10 ns. Em seguida foi realizada uma etapa de equilíbrio NPT por 20 ns em 300 K e uma etapa de produção, em que o sistema evoluiu por 110 ns com passo temporal de 2 fs. Os resultados foram analisados utilizando ferramentas do Amber16⁵.

RESULTADOS E DISCUSSÃO

Inicialmente foram realizadas análises estruturais de ambas as micelas na presença e ausência de ânions. Os resultados obtidos mostram que a micela HPE possui estrutura mais estável que a micela HPC quanto à forma. O contato com íons provoca apenas um empacotamento no tamanho da micela HPE,

insensível ao tipo de ânion adsorvido no sistema, enquanto para a micela HPC, a presença de ânions afeta as propriedades estruturais, dependendo do tipo de ânion adsorvido. Para analisar a adsorção dos ânions na interface, foram analisadas as funções de distribuição radial (RDF) dos ânions relativos à superfície da micela. Observamos que, por apresentar um grupo polar, [–N(CH₃)₃]⁺, com caráter hidrofóbico, a adsorção na micela HPC segue a série direta de Hofmeister, em que ânions percloratos (grandes e menos hidratados) foram observados em maior quantidade, como esperado. Já na micela HPE, ocorre o oposto. Devido à hidrofilicidade do grupo polar, o padrão de adsorção na interface micela HPE/solução é inverso à série de Hofmeister. Foi observado nesta interface a presença de ânions fluoretos (pequenos e mais hidratados) em maior quantidade. Como a HPE é composta por uma superfície bastante polar e hidrofílica, [–N⁺H₃]⁺, é observada uma inversão na série de adsorção de ânions e uma especificidade menos pronunciada. Visto que a única diferença entre as duas micelas é o grupo polar mais externo e corroborados em outros estudos^{2,3}, podemos afirmar que nestes sistemas, os efeitos hidrofóbicos e hidrofílicos da superfície determinam diretamente a ordem direta e inversa da série de Hofmeister. Deve-se ressaltar que, usando campo de forças atomístico, é possível reproduzir os efeitos de interação das cargas na superfície. Sendo assim, não é necessário, nesses casos, a utilização de campos de forças polarizados ou de inclusão de efeitos de dispersão para reproduzir as observações experimentais.

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Potential curve for a Lithium molecule confined by prolate spheroidal boxes

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Keywords: Molecular Confinement, Lithium molecule, Variational Method, Molecular Orbital, Potential Curve.

Intro

The spatial confinement of atoms and molecules affects the physical and chemical properties of these systems. The results of this confinement are observed in different situations, such as, high-pressure systems, zeolites and nanotubes [1].

In this work, the lithium molecule is confined in a prolate spheroidal cavity. In this way, the ground state potential curve is obtained by using the variational method.

The results for the confined molecule show that the potential curve minimum is more prominent compared with the free one. The internuclear equilibrium distance also changes under confinement environment.

Method

For the confined Li_2 molecule in the Born-Oppenheimer approximation the Hamiltonian in atomic units is given by:

$$\hat{H}_{\text{He}_2} = - \sum_i^6 \frac{1}{2} V_i^2 - \sum_i^6 \left(\frac{3}{r_{Ai}} + \frac{3}{r_{Bi}} \right) + \sum_{i,j > i} \left(\frac{1}{r_{ij}} \right) + \frac{9}{R} + V_c, \quad (1)$$

the indices A and B refer to nuclei, $r_{A,B}$ represents the distance between electron and the nuclei, R is the distance between the nuclei and V_c is the confined potential, which is adopted as zero inside the cavity and infinity outside.

The trial function is given by the Slater determinant, thus, the close-shell Hartree-Fock energy described by the molecular orbitals $1s\sigma$ (bonding), $1s\sigma^*$ (anti-bonding) and $2s\sigma$, the is given by [2]:

$$\langle \hat{H}_{\text{Li}_2} \rangle = 2\langle 1s\sigma | \hat{h} | 1s\sigma \rangle + 2\langle 1s\sigma^* | \hat{h} | 1s\sigma^* \rangle + \quad (2)$$
$$2\langle 2s\sigma | \hat{h} | 2s\sigma \rangle + \sum_{i,j} (2J_{ij} - K_{ij}) + \frac{9}{R},$$

where \hat{h} is the operator related to the one electron integrals, first two term of Eq. (1), J and K are the Coulomb and Exchange integrals.

The molecular orbitals, in prolate spheroidal coordinates, are given by [3]:

$$\psi_{1s\sigma} \propto (\xi_c - \xi) e^{-\mu_0 \xi} \cosh(\beta_0 \eta), \quad (3)$$

$$\psi_{1s\sigma^*} \propto (\xi_c - \xi) e^{-\mu_0 \xi} \sinh(\beta_0 \eta) \text{ and}$$

$$\psi_{2s\sigma} \propto (\xi_c - \xi) (2 - \xi - a_{2s\sigma, 1s\sigma}) e^{-\mu \xi} \cosh(\beta \eta),$$

where μ_0, β_0, μ and β are variational parameters, $a_{2s\sigma, 1s\sigma}$ is obtained from orthogonality condition $\langle \psi_{1s\sigma} | \psi_{2s\sigma} \rangle = 0$. The term $(\xi_c - \xi)$ imposed that the trial function is equal to zero for $\xi = \xi_c$.

Results

Usually, for confined molecules the major axis ($R\xi_c$) is chosen as the confinement parameter. Thus, the major axis is fixed and the distance between the nuclei are allowed to change. In the approach used here, the nuclei are fixed at the foci, so a change in the internuclear distance leads to a variation in the eccentricity of the ellipsoid. In this case, the internuclear equilibrium distance represents the cavity that minimizes the energy. In figure 1 the potential curve for the confined lithium molecule is showed for each value of major axis.

For smaller values of major axis ($R\xi_c$), the potential curves change. For strong confinement (for example, $R\xi_c=10$) the curve is not characterized as the Morse like potential. On the other hand, for large values of the major axis the potential curve return to free case (Morse potential).

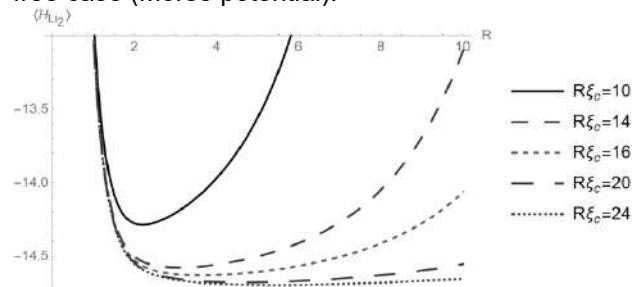


Figure 1: Potential curve for each value of major axis.

It is possible to note that the internuclear equilibrium distance (R_{eq}) changes in terms of the confinement parameter. The value of R_{eq} decreases to small values of $R\xi_c$. In case of major axis increase, the value of R_{eq} converges to the free molecule. For $R\xi_c=24$, the value found is $R_{eq}=5.4053$ bohr radius, which is indicated in reference [4] for free molecule ($R_{eq}=5.37$ bohr radius).

Conclusions

The results show that the potential curves (Figure 1) change when the system is confined by an infinite barrier.

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Estudo Químico quântico do potencial antioxidante do carvacrol

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Palavras-Chave: Carvacrol, antioxidante, DFT.

INTRODUÇÃO

Os óleos essenciais obtidos das plantas, possuem forte atividade biológica devido a seus altíssimos teores de monoterpenos e compostos oxigenados [1]. O carvacrol é um fenol monoterpênico presente em óleos essenciais, com uma grande variedade de propriedades farmacológicas e biológicas, o que inclui a atividade antioxidante [2]. O potencial antioxidante está diretamente relacionado aos parâmetros eletrônicos: energia total (E); energia de ionização (EI); energia de dissociação da ligação O-H (EDL); orbital molecular ocupado de mais alta energia (HOMO) e cargas atômicas parciais [3].

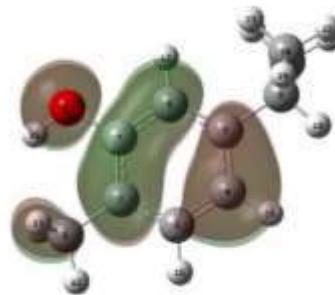


Figura 1. Representação gráfica do orbital molecular ocupado de mais alta energia (HOMO).

METODOLOGIA

O método da teoria do funcional da densidade (DFT/B3LYP) com a função de base 6-31++G(d,p) foi usada na otimização da geometria molecular, e na obtenção dos parâmetros eletrônicos. Todos os cálculos foram realizados no programa Gaussian 2009.

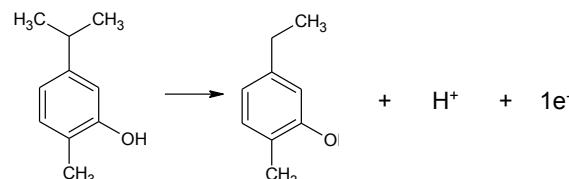
RESULTADOS

A tabela 1 apresenta os resultados obtidos para a energia total (E), energia de ionização (EI) e a energia de dissociação da ligação O-H (EDL). Esses valores encontrados, mostram a estabilidade da reação de oxidação do carvacrol.

Tabela 1. Energia total (E), Energia de dissociação da ligação O-H (EDL) e de ionização para o carvacrol (EI).

E (a.u)	EDL (kcal/mol)	EI (kcal/mol)
-464,7696	401,55	178,99

A figura 1 apresenta o HOMO do carvacrol no estado fundamental. Observa-se nesta imagem, que os orbitais localizados nos átomos C1, C2, C4, C5, C8, C10 e O11 possuem contribuição para formação do HOMO. O cálculo das cargas atômicas parciais NBO no carvacrol neutro e oxidado, revelou maior variação da densidade de carga no oxigênio (-0,71 → -0,21), portanto, haverá uma saída de elétron no oxigênio, e na sequência a saída de H⁺, formando o radical, como mostra o mecanismo proposto no esquema 1.



Esquema 1. Mecanismo proposto para a oxidação do carvacrol.

CONCLUSÕES

Os resultados obtidos para as energias total, ionização e dissociação, revelam a estabilidade da reação de oxidação do carvacrol. A obtenção do HOMO e das cargas atômicas, indicou o átomo de oxigênio, como o provável local de oxidação

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The Overlooked Role of Pauli Repulsion in the Gauche Effect

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Keywords: Density functional calculations, hyperconjugation, steric Pauli repulsion.

The so-called *gauche* effect is the phenomenon that describes the preference for *gauche* over the *anti*-conformer along a 1,2-disubstituted ethane fragment (*i.e.*, X-C-C-X) in cases where X is an electron-withdrawing group (see Figure 1a).^[1] The *gauche* effect has been widely used as a tool to control the conformational preference of organic molecules to afford them specific molecular properties.^[2]

In the currently accepted model, the *gauche* effect arises from stabilizing hyperconjugative interactions between antiperiplanar σ orbitals (see Figure 1b).^[3] However, other theories propose the role of other forces behind conformational preferences.^[4]

Herein,^[5] we investigate the origin of the *gauche* effect within the framework of quantitative Kohn-Sham molecular orbital (KS-MO) theory using the series of 1,2-dihaloethanes XH₂C-CH₂X (X = F, Cl, Br, I). The Activation Strain Model (ASM) along with

the matching, canonical Energy Decomposition Analysis (EDA)^[6] are employed to unravel the physical factors underlying the conformational trends.

Comprehensive analysis along the rotational potential energy surface reveals that, at variance to the hyperconjugation model, the switch in preference from *gauche* for X = F to *anti* for X = Cl, Br, and I is caused by the increasing steric demand of the substituent X on descending group 17. We show that hyperconjugative orbital interactions always favor *gauche*. Only in the case of the relatively small fluorine atoms, steric (Pauli) X···X repulsion is small enough to not overrule the *gauche* preference set by hyperconjugation. For larger halogens, steric repulsion destabilizes the *gauche* conformer and, in this way, shifts the energetic preference from *gauche* to *anti*.

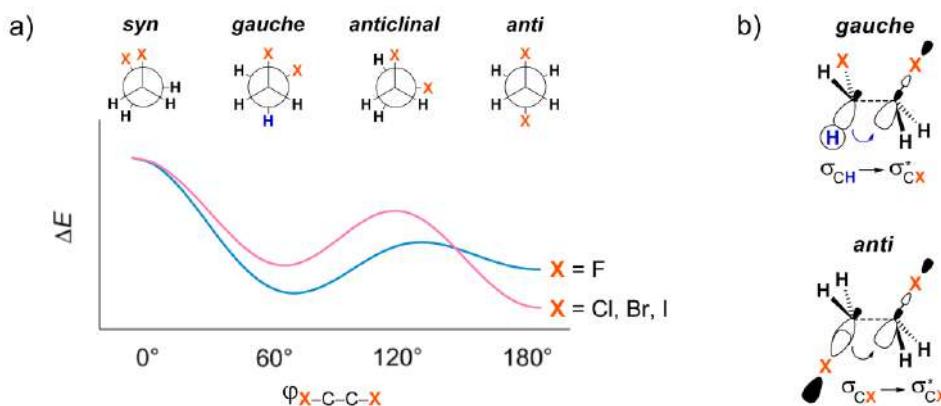


Figure 1. a) Stationary points in the energy profile for rotation around the C-C bond of 1,2-dihaloethanes and b) main orbital interactions affecting the *gauche-anti* equilibrium.

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Theoretical analysis of curcumin metal-chelated derivatives as dyes for DSSC devices

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Key words: Curcumin; metal chelation; TD-DFT.

Abstract:

Curcumin is a natural compound extracted from plant *Curcuma longa*, which has been studied in the last few years for its relevant biological properties [1,2]. Recent applications include prevention of Alzheimer's disease and cancer treatment through Photodynamic Therapy (PT), using curcumin molecules alone or chelated to transition metals [3,4]. These species present interesting features as extended π-conjugated systems and strong absorption transitions mainly in the UV-visible region of the electromagnetic spectrum. Although PT technique explores these light absorption properties, this molecule has not been tested yet for other light-absorbing purposes, as dyes in DSSC devices. In this work we performed a theoretical study to investigate the potential of these complexes as dyes for energy conversion purpose.

Methodology: We performed optimization and frequency calculations to determinate minimum conformational energies for several transition metals (Co, Cr, Cu, Fe, Ni, Ru, Zn) coordinated to a curcumin molecule (1:1). Simulations were based on the Density Functional Theory (DFT) method [5,6] and performed with Gaussian 09. To estimate displacements in pure curcumin's absorption spectrum and to evaluate the excited state properties of these compounds, we also performed time-dependent DFT (TD-DFT) calculations. These simulations included comparisons among functionals with diverse Hartree-Fock electronic exchange percentage (M06L, M06X, ωB97XD, CAM-B3LYP), using always the same basis set, in order to explore the influence of the electronic exchange description in these systems.

Results: We obtained minimum energy conformations for all the species. Outputs showed that metal chelation may displace the main absorption peak of curcumin in different ways. Redshifts occurred for Co, Cu and Zn compounds and blueshifts for Cr, Fe and Ru compounds. No great differences in the general aspect of the spectrum were observed for Ni and Zn complexes. Furthermore, plots of the frontier orbitals (HOMO-1, HOMO, LUMO and LUMO+1), confirm metal-to-ligand charge transfers (CT) for all complexes and confirm a single ligand-to-metal CT for spin B HOMO → LUMO transition in Copper complex [7]. No charge

transfer between metal and curcumin was observed for the Zn complex.

Conclusions: Results up to now indicate that all metal complexes present potential as dyes for DSSC applications, as several metal-to-ligand charge transfers were observed. As for the different functionals, comparison with experimental results suggest that range-separated functionals best describe the electronic properties of these compounds. Next steps include the theoretical evaluation of these compounds in solvated media.

Acknowledgements: This work was supported by CNPq, CAPES, and FAPESP agencies.

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Supercooled DNA hydration water: dynamical and structural aspects

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Palavras-Chave: Nucleic acids, dynamical transition, diffusion.

Introduction

Water exhibits several anomalies, such as unusual high melting, boiling and critical points, non-monotonical dependence of density, heat capacity and compressibility on temperature, among several others. Water has also a very reach phase diagram, can be easily supercooled and exhibits amorphous states. Many of the water anomalies are enhanced in the presence of biomolecules and indeed they seem to play an important role to the function of these biomolecules. Nucleic acids are versatile biomolecules and due to their complex structure with high charge density and solvent exposed surface, the interaction with water is extremely relevant to their structure and behavior. Recently, a slowing down of the dynamics of water in the vicinity of DNA was found [1], as well a dynamical transition. Besides, the water structure in this environment was found to be largely amorphous.

Methods

We investigate, using MD simulations, the behavior of DNA hydration water and its dependence on the water model. We compare some of the four-center water models of the TIP family – TIP4P [2], TIP4P-Ew [3], TIP4P/ICE [4] and TIP4P/2005 [5] – solvating the Dickerson-Drew DNA dodecamer d(CCGAATTCGCG)2. MD-NPT simulations using GROMACS were carried out from temperatures ranging from 300 K down to 220 K. We analyzed bulk water and also the hydration water around the minor and major groove. Radial distribution function, mean square displacement and diffusion coefficient were calculated.

Results

The radial distribution function of bulk water shows that the TIP4P-Ew and TIP4P/2005 water models capture the water structure slightly better than the original TIP4P parameters, which on its side remains better than the TIP4P/ICE. The radial distribution function of water hydrating the minor or major groove shows two well defined peaks at 0.25 and 0.4 nm, corresponding to a primary and a secondary shell, enabling the definition of the set of hydrating water for further analysis (this set is dynamical and the water molecules belonging to it updated during the simulation). The analysis of the RMSD of water molecules in the bulk region and hydrating the minor or major grooves showed that there was a slowing down of the dynamics due to the interaction with the nucleic acid, in the minor or major grooves. Besides, a diffusion anomaly with a deviation from Fickian

behavior (RMSD linear with time) was found for low temperatures and short time scales in the case of TIP4P-Ew and TIP4P/2005. In the long time scales the Fickian behavior was recovered, enabling to calculate a diffusion coefficient. The diffusion coefficients of bulk water for the TIP4P-Ew and TIP4P/2005 water models showed remarkable agreement with the experiment, but a large slowing down was found for water hydrating the DNA Grooves. An Arrhenius plot (logarithm of diffusion coefficient against reciprocal temperature) shows non-linear behavior and a clear separation between the high-temperature and the low-temperature regimes, pointing out to a dynamical transition at low temperatures.

Conclusions:

Water molecules in the Grooves of DNA show a remarkable different behavior than in the bulk, but the quantitative differences are strongly dependent on the water model used. The influence of the biological environment is strong at temperatures below 250 K for TIP4P/2005 and TIP4P/Ew water models, a hint of a dynamical transition. Besides, even at room temperatures the interaction or confinement-induced slowing down is noticeable. The glassy nature of water, however, demands a further careful study on the structure

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Identificação de inibidores simultâneos de PARP1, Bcl-2 e Bcl-xL através de estudos computacionais

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Palavras-Chave: química medicinal, docagem, terapia direcionada

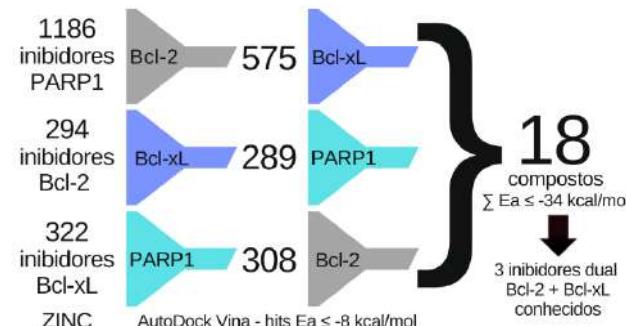
A PARP1 é uma enzima que atua no reparo de danos de DNA, sendo sua inibição um método importante no tratamento de diversos tipos de câncer. Sua aplicação no manejo do Sarcoma de Ewing (um tipo de câncer ósseo pediátrico cujo prognóstico é ruim para casos disseminados da doença - SE) ainda é incipiente, principalmente devido à resistência em pacientes altamente pré-tratados.¹ Em 2019, Heisey *et al.* demonstraram que células de SE ingênuas respondiam melhor ao olaparibe (inibidor de PARP1) do que células do mesmo paciente após tratamento citotóxico. Além disso, descobriram que a falta de morte celular significativa era mediada pelas proteínas antiapoptóticas Bcl-2 e Bcl-xL, sendo sua inibição suficiente para retomar a atividade do olaparibe em células resistentes e aumentá-la em células ingênuas. De fato, membros da família BCL-2 regulam a resposta apoptótica e demonstraram ser causa de resistência tanto na terapia citotóxica quanto na direcionada.² Desse modo, a descoberta de inibidores de PARP1 que também inibam Bcl-2 e Bcl-xL pode gerar novas alternativas de tratamento para SE e outros cânceres em que PARP1 é um alvo.

Neste trabalho, utilizou-se a base de dados ZINC³ para obtenção de compostos com IC_{50} ou $K_i \leq 10 \mu M$ para os três alvos de interesse, recuperando-se 1802 estruturas 3D otimizadas, prontas para *docking*, em formato mol2. Em seguida, o programa Raccoon⁴ foi utilizado para separar as moléculas em arquivos individuais e realizar a conversão para o formato pdbqt com adição de hidrogênios polares, cálculo de cargas e definição de ligações rotáveis.

O AutoDock Vina⁵ foi utilizado para realizar a varredura virtual dos compostos através de *docking* molecular. Para isso, a região de busca e outros parâmetros foram otimizados a fim de se reproduzir as poses dos ligantes originais das estruturas das proteínas disponíveis no PDB (PARP1: 7KK5, Bcl-2: 6QGG, Bcl-xL: 7JGW), obtendo-se RMSD de 0,881 Å para PARP1, 1,17 Å para Bcl-2 e 0,483 Å para Bcl-xL. Os inibidores experimentais foram docados nos seus alvos originais, a fim de se estabelecer um bom valor de afinidade de corte. Foi possível observar que mais de 85% dos compostos conhecidamente ativos frente à PARP1 e 95% dos ativos para Bcl-2 ou Bcl-xL apresentaram energia de afinidade (E_a) ≤ -8 kcal/mol. Sendo assim, este valor foi considerado o ponto de corte para os *hits*.

Os compostos, então, foram avaliados através de uma metodologia de *docking* cruzado,

ilustrada na figura abaixo. Os inibidores de PARP1 foram docados na estrutura da Bcl-2, os da Bcl-2 docados na Bcl-xL e os da Bcl-xL na PARP1. Os compostos que apresentaram $E_a \leq -8$ kcal/mol passaram para a próxima etapa de varredura, sendo docados no alvo restante. Por fim, 18 compostos foram selecionados por apresentarem a soma das E_a com os três alvos inferior ou igual a -34 kcal/mol.



Destes 18 compostos, três já possuíam atividade experimentalmente determinada frente à Bcl-2 e Bcl-xL simultaneamente e outros três foram previstos como inibidores simultâneos destas duas proteínas pela plataforma CHEMBL, validando de forma promissora esta metodologia.

Entre os próximos objetivos do trabalho estão a modelagem dos loops distantes do sítio ativo faltantes nas estruturas dos alvos proteicos e a simulação por dinâmica molecular utilizando o pacote GROMACS a fim de se analisar com mais detalhes a interação proteínas-ligantes, bem como estimar o ΔG de interação, para se escolher os melhores candidatos a testes de inibição.

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Intermolecular Covalent Interactions: A Unified Framework for Pnictogen-, Chalcogen-, Halogen-, and Hydrogen Bonds

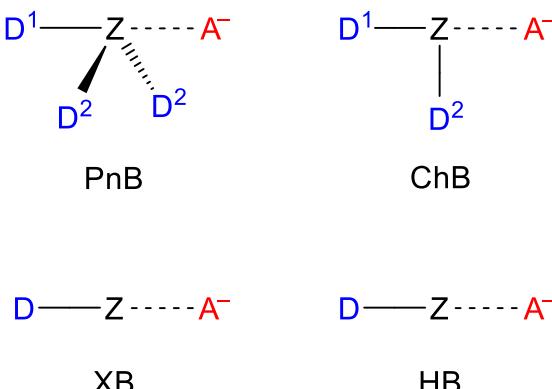
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Palavras-Chave: *Intermolecular interactions, Bond theory, Density functional calculations.*

Pnictogen bonds (PnB), chalcogen bonds (ChB), halogen bonds (XB), and hydrogen bonds (HB) are intermolecular interactions formed by the coordination of a Lewis base (A), or nucleophile, and a Lewis acid (D_mZ , Z = Pn, Ch, X, H; see Scheme 1), resulting in a $D_mZ \cdots A^-$ complex.^[1,2,3] The intermolecular interactions are the subject of investigation due to their application in several fields of chemistry and biochemistry, including supramolecular, catalysis, and drug design.^[4]



Scheme 1. Pnictogen- (PnB), Chalcogen- (ChB), Halogen- (XB), and hydrogen-bonded (HB) $D_mZ \cdots A^-$ -model complexes (Z = Pn, Ch, X, H; Pn = N, P, As, Sb; Ch = O, S, Se, Te; X = F, Cl, Br, I; D, A = F, Cl, Br).

Herein, we provide a unified framework to understand PnB, ChB, XB, and HB. This has emerged from the quantum chemical investigation of a wide range of archetypal $D_mZ \cdots A^-$ complex (Z = Pn, Ch, X, H; D, A = F, Cl, Br; see Scheme 1) using relativistic density functional theory (DFT) at ZORA-M06/QZ4P. Our quantitative Kohn-Sham molecular orbital (KS-MO) theory and canonical energy decomposition analyses (EDA)^[5] reveal that these intermolecular interactions have a significant covalent component.^[1,2,3] We have amassed sufficient evidence to challenge the σ -hole model, which erroneously suggests that these bonds are essentially electrostatic in nature.^[6] In fact, the σ -hole

model would only be conceptually correct if the bond donor (D_mZ) were a 2D surface with an electrostatic potential and the bond acceptor (A) a point charge, which is far from the physical reality.

We conclude that the commonly accepted designation "Non-Covalent Interaction (NCI)" for the studied intermolecular interactions does not appropriately describe their nature and should be replaced by the more precise designation of "Intermolecular Covalent Interaction (ICI)".

Acknowledgments

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Aplicando o Modelo do Eletrodo de Hidrogênio Computacional para Análise da Reação de Redução de Oxigênio pelo Mecanismo de 2 Elétrons em Superfícies de CeO₂

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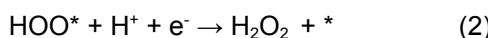
Palavras-Chave: Óxido de cério, peróxido de hidrogênio, teoria do funcional da densidade.

Introdução

A reação de redução de O₂ para H₂O₂ é promissora para aplicação no tratamento de águas, visando à remoção de disruptores endócrinos [1]. O CeO₂ é um material que exibe alto rendimento e seletividade para essa reação [2]. Utilizou-se o modelo do eletrodo de hidrogênio computacional (CHE)[3] para determinar a contribuição de diferentes superfícies[4] na atividade catalítica.

Metodologia

Foram selecionadas para esse estudo as superfícies (100), (110), (111), (221) e (331), considerando-se os sítios não equivalentes em cada. As moléculas gasosas (H₂, H₂O e H₂O₂) e seus valores experimentais são utilizados como referência. O mecanismo de reação é descrito conforme as equações seguir:



A variação de energia livre de Gibbs é dada por:

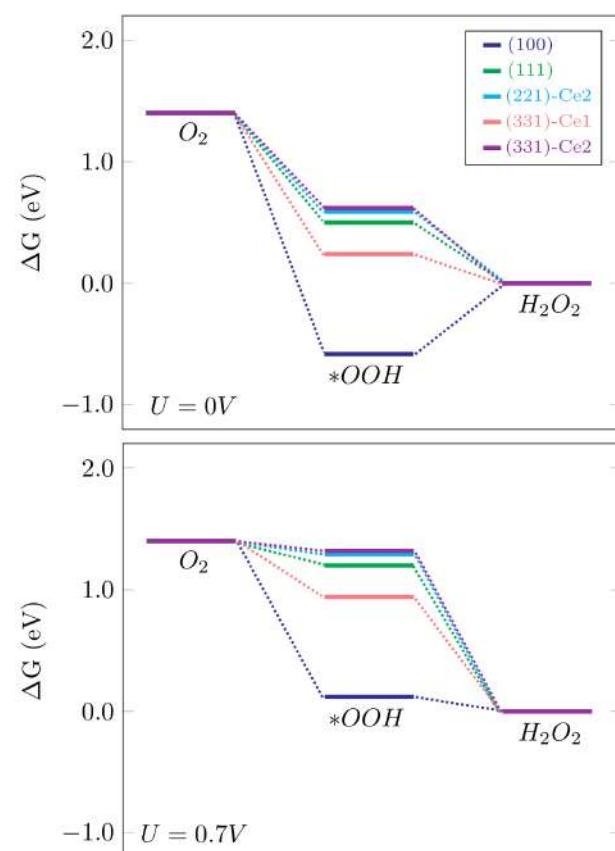
$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_{pH} - neU \quad (3)$$

onde ΔE é a energia de adsorção obtida com cálculos de DFT, $\Delta ZPE - T\Delta S$ descrevem as contribuições vibracionais e entrópicas, ΔG_{pH} a correção para pH ≠ 0, U a ação de um potencial sobre uma reação envolvendo n elétrons.

Resultados e Conclusão

A adsorção da espécie intermediária (*OOH), fator chave para o mecanismo de 2 elétrons, é favorável em todos os sítios considerados. A molécula de H₂O₂, por sua vez, não adsorve em (110), (221)-Ce1 e (221)-Ce3. O diagrama de energia livre de Gibbs foi construído para os sítios nos quais a molécula de H₂O₂ é estável, ou seja, desconsiderando (110), (221)-Ce1 e (221)-Ce3, conforme a figura 1 a e 1 b a seguir. É possível notar que a reação é termodinamicamente favorável ($U = 0$ V), indicado pelo decréscimo em energia na etapa intermediária. Além disso, sob ação do máximo potencial permitido, de equilíbrio dessa reação ($U = 0,7$ V), nenhuma superfície apresenta uma variação positiva de energia livre de Gibbs. Isso indica que a

reação de interesse é favorável em todas as superfícies consideradas neste estudo em pelo menos um sítio da rede, especialmente na (100).



Coordenada de Reação

Figura 1: Variação de energia livre de Gibbs para (a) U = 0 V e (b) U = 0,7 V em superfícies e sítios favoráveis para a formação de H₂O₂.

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Planejamento por Modelagem e Dinâmica Molecular de Polímeros Adsorsores de Pesticidas Organofosforados

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Palavras-Chave: Polímeros, Pesticidas Organofosforados, Dinâmica Molecular.

INTRODUÇÃO

O Brasil é um dos maiores exportadores de alimentos do mundo. A alta produtividade agrícola é acompanhada pelo uso expressivo de pesticidas nas plantações, com destaque para o grupo dos pesticidas organofosforados (Ops), considerados altamente tóxicos aos mamíferos, e causa de riscos ao meio ambiente, advindos da contaminação do solo, ar e especialmente da água. Assim, neste trabalho, foram empregadas técnicas de modelagem e dinâmica molecular (DM) para o estudo das interações inter e intra moleculares, em função do tempo, de oligômeros de polímero modificado e moléculas dos Ops mais utilizados no Brasil, a fim de investigar a capacidade de adsorção dos Ops pelos oligômeros propostos em solução aquosa.

MATERIAL E MÉTODOS

O programa Avogadro foi utilizado para modelar dois tipos de oligômeros derivados do polietileno com a inserção dos aminoáricos presentes na tríade catalítica da enzima acetilcolinesterase (AChE), constituídos de 25 meros cada, denominados PE01 e PE02. Os pesticidas selecionados, acefato, clorpirimifós, glifosato, malation e terbufós, e os oligômeros, foram otimizados com o método semiempírico PM7 no programa MOPAC, com posterior parametrização, tanto dos oligômeros quanto dos Ops, utilizando o ACPYPE e o MKTOP. Os sistemas oligômeros-Ops foram gerados com o Packmol e imersos em caixas dodecaédricas solvatados com moléculas de água e submetidos a 50ns de DM com o Gromacs. As trajetórias das simulações foram analisadas pelo Desvio da Raiz Média Quadrática, Raio de Giro, Área Superficial Acessível ao Solvente e energia livre de interação ($\Delta G_{\text{interação}}$) de cada sistema simulado.

RESULTADOS

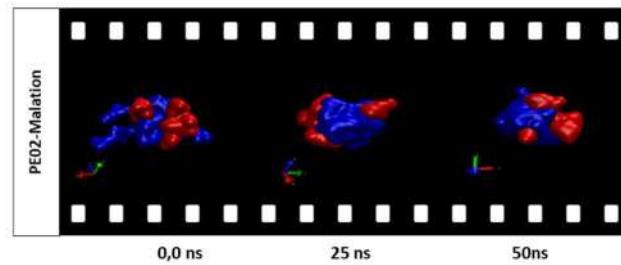
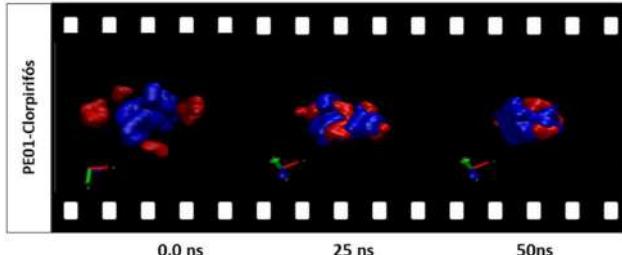


Figura 01 - Mudança de posicionamento dos melhores resultados de $\Delta G_{\text{interação}}$ dos sistemas oligômero-Ops. Imagens geradas pelo programa VMD.

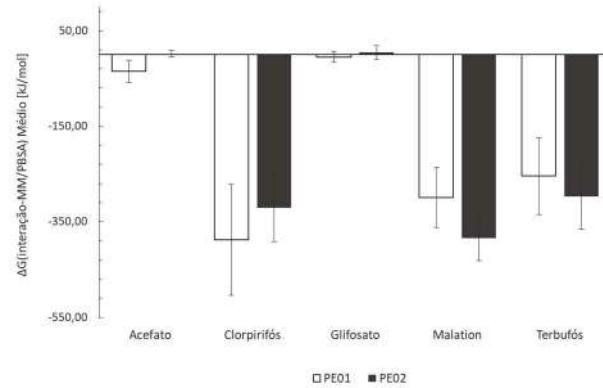


Figura 02 – Gráfico de barras dos resultados médios de $\Delta G_{\text{interação-MM/PBSA}}$ e desvio padrão dos sistemas PE01-Ops e PE02-Ops.

CONCLUSÃO

Todos os sistemas mostraram comportamento relativamente estáveis após cerca de 5ns de DM. O oligômero PE01 interage melhor com os pesticidas acefato, glifosato e clorpirimifós, dentre estes, o melhor resultado de $\Delta G_{\text{interação}}$ é referente ao sistema PE01-clorpirimifós, enquanto o oligômero PE02, mostrou melhor interação com os pesticidas malation e terbufós, e o melhor resultado obtido foi para sistema PE02-malation.

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Simulating X-ray Photoelectron Spectra using Multireference Algebraic Diagrammatic Construction Theory

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Keywords: Electronic Structure Methods, X-ray Spectroscopy, Multireference Quantum Chemistry

X-ray spectroscopic techniques have been widely applied and developed to investigate electronic structure and dynamics in chemical systems and materials. The development of new *ab initio* methods to simulate X-ray excited states is essential to improve the understanding of core electron phenomena, especially for multireference systems, which require proper wave functions to be correctly described. In the present work, we propose and implement the algebraic diagrammatic construction (ADC) in the multireference (MR) framework^[1] for core ionization potentials. The MR-ADC method uses a multiconfigurational wavefunction as a reference (e.g., CASCI or CASSCF), from which the excited states are calculated. The generalized eigenvalue problem is given by

$$M_{\pm} Y_{\pm} = S_{\pm} Y_{\pm} \Omega_{\pm}$$

where M is the effective Liouvillean matrix, S is the overlap matrix, and Ω and Y are the eigenvalues and eigenvectors, respectively. Unlike other multireference methods, the MR-ADC does not require additional orbitals in the reference active space to achieve their related excitations. The extended second-order formulation for valence electrons ionization (IP-MR-ADC(2)-x) presents mean absolute errors of 0.3 eV predicting ionization potentials of small molecules at equilibrium and stretched geometries^[2].

Electronic core excited states bring further computational challenges. Standard numerical approaches for eigenvalue equations are infeasible due to the requirement of computing all energetically lower-lying excited states in advance. Therefore, we implemented the Core-Valence Separation (CVS) approximation to

the IP-MR-ADC framework to compute core ionization potentials. This approximation enables access to the inner-shell excitations decoupling them from the complete configurational space (Figure 1). It directly reduces the computational costs, decreasing the size of the M matrix.

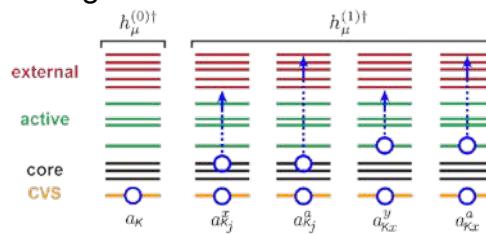


Figure 1. Representation of electronic excitations included in the CVS-IP-MR-ADC method.

We investigated the photoelectron spectra of transition metal complexes using the CVS-IP-MR-ADC to obtain their core ionization potentials and satellite peaks. Table 1 presents preliminary results obtained for the Cr(CO)₆ molecule in Cr, C, and O elements edges. Both variants of IP-MR-ADC show good agreement with experiments, except in the case of the Cr 2s⁻¹ shell, which shows a particular limitation of the CVS approximation.

Table 2. Core ionization potentials of Chromium Hexacarbonyl molecule. Calculations done using CASSCF(6,8) as ground-state reference and Def2-SVP basis set with exact-two-component (X2C) approach for scalar relativistic effects.

Shell	CVS-IP-MR-ADC(2)	CVS-IP-MR-ADC(2)-x	Exp. ^[3]
Cr 2s ⁻¹	713.3	710.0	703.2
Cr 2p ⁻¹	594.3	592.3	590.8
Cr 3s ⁻¹	85.4	84.8	82.2
Cr 3p ⁻¹	50.0	49.6	51.1
C 1s ⁻¹	298.0	296.3	293.2
O 1s ⁻¹	541.4	542.2	539.6

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Machine Learning Applied to the Sensitivity of Explosives

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Explosives are substances or mixtures capable of chemically transforming into gases with extraordinary speed and heat production that generate high pressures [1]. One way to quantify the sensitivity of an explosive is to measure the sensitivity to impact h_{50} , defined as the height in centimeters that half of the drops of a standard hammer ignites the explosive [2].

In this work, sensitivity values of nitroaromatic explosives were determined using Machine Learning (ML) algorithms, having as input data properties of the molecular charge density [2] and structural data. An example of a nitroaromatic explosive is the TNT, depicted in FIG. 1.

To predict the h_{50} impact sensitivities of this family of widely used explosives [3], we employed a ML technique known as supervised learning, since experimental h_{50} values are used as the target attribute in the training set.

For a set of 50 molecules, properties derived from the distributed multipole analysis (DMA) were used, calculated from DFT/B3LYP//6-311+G* optimized geometries. In the DMA method, the charge density of a molecule is decomposed into atom-centered electric multipoles (monopoles, dipoles, quadrupoles) [4]. This method provides an accurate description of the charge density that has a direct chemical interpretation [2].

The following computed DMA multipole values and structural parameters comprised the set of properties used as input to the algorithms: the sum of the monopole values of the atoms of the nitro group $Q_0(NO_2)$, the sum of the dipole values of the atoms of the nitro group $Q_1(NO_2)$, the sum of the quadrupole values of the atoms of the benzene ring $Q_2(ring)$ and the amount of nitro groups attached to the benzene ring. The nitro group is an explosophore group because it gives explosive properties to these molecules.

Three out of 41 algorithms that were tested showed good performance for the training set: Extra Trees, Random Forest, and Gradient Boost [5]. In the test group, however, only the first two gave good results. The choice of the most promising algorithms was initially based in Ref. [6], and then refined by using the Python library Lazy Predict, which analyses the training set employing default values for the hyperparameters of the ML algorithms implemented in the Scikit-learn library.



FIG. 1 - TNT

To improve the performance of the algorithms, lists were created with different values of their hyperparameters, and the best combinations were checked using a Grid Search technique.

In our test set, sensitivity values were predicted with a mean square error (RMSE) of 28.9 cm and 29.6 cm for the Random Forest and Extra Trees algorithms, respectively. The aforementioned DMA multipoles and structural properties used to describe the explosive molecules lead to the best predictions of the h_{50} values. From a chemical point of view, this means that charges (a measure of charge localization) and dipoles of the nitro group (a measure of polarization), and the quadrupole values of the benzene ring (a measure of electron delocalization), as well as the number of NO_2 explosophore groups, proved to be the most important for this task.

FIG. 2 presents some of the results found in the test group for the best two ML algorithms.

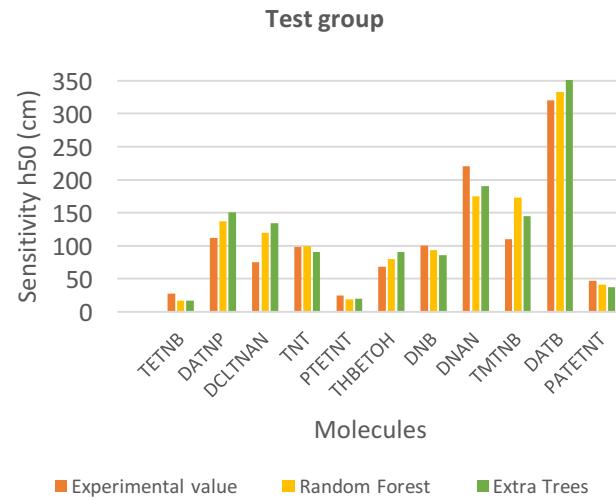


FIG. 2 – Test group results

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Quasiclassical Trajectory Study of C+C₂ Isotopic-Exchange Reactions: From Theory to Applications in Astrochemistry

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Keywords: quasiclassical trajectory, potential energy surfaces, astrochemistry.

1) Introduction

Our current understanding of interstellar carbon isotopic fractionation in molecular clouds hinges on the interpretation of astrochemical kinetic models¹. Yet, the various isotopic-exchange reactions included carry large uncertainties in their estimated rate coefficients, notably those involving¹ C+C₂.

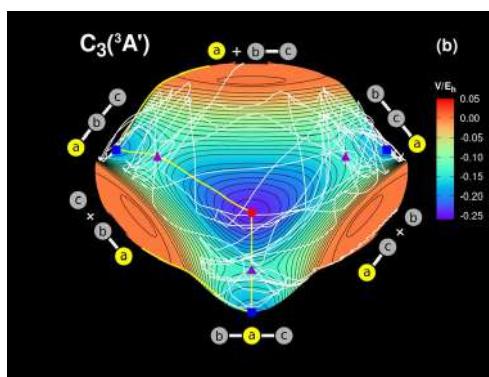
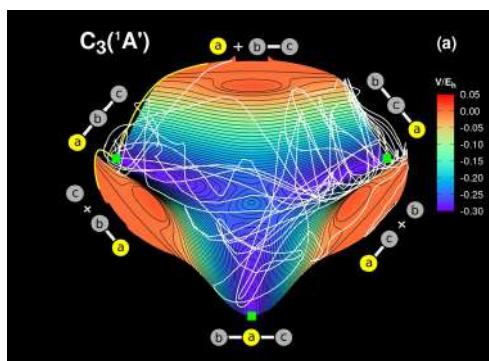
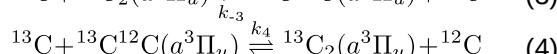
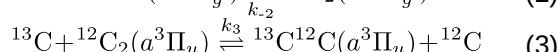
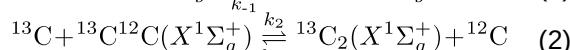
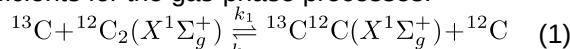


Figure 1: 3D plots of the PESs of (a). C₃(¹A') and (b). C₃(³A'). White lines show sample reactive trajectories.

By employing the global potential energy surfaces (PESs) of ²C₃(³A') and ²C₃(¹A') and a variation of the quasiclassical trajectory (QCT) method⁴, this work aims at providing accurate theoretical rate coefficients for the gas-phase processes:



2) Theoretical Methods

Using the VENUS96C QCT code⁴, batches of 10⁴ trajectories were run for the ground adiabatic ¹A' and ³A' PESs separately; see Figure 1. The thermal rate coefficients were calculated as⁴

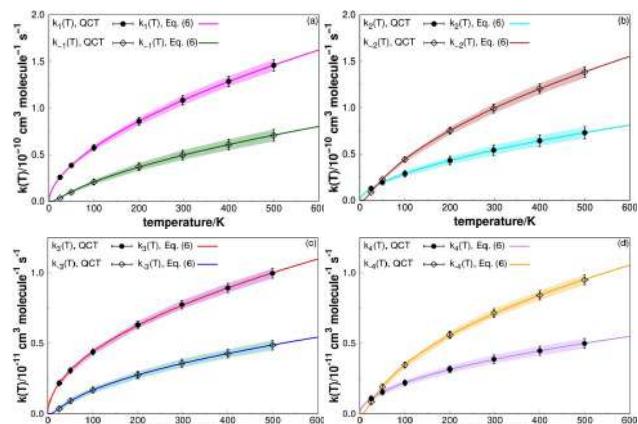


Figure 2: Forward and reverse thermal rate coefficients for reactions (1)-(4) and associated error bars.

$$k(T) = g_e(T) \left(\frac{8k_B T}{\pi \mu_{\text{C}+\text{C}_2}} \right)^{1/2} \pi b_{\max}^2 \frac{N_r}{N} \quad (5)$$

where N_r is the number of reactive trajectories out of a total of N that were run, $\mu_{\text{C}+\text{C}_2}$ is the reactants reduced mass, b_{\max} the maximum impact parameter and g_e(T) is the electronic degeneracy factor.

3) Discussion & Summary

Figure 2 shows the calculated forward and reverse rate coefficients for the reactions (1)-(4) within 25 ≤ T/K ≤ 500. Such QCT data have also been fitted to the three-parameter relation⁵

$$k(T) = A \left(\frac{T}{298.15} \right)^B \exp \left(\frac{-C}{T} \right) \quad (6)$$

where A, B, and C are adjustable parameters. As noted, the k's show a positive temperature dependence¹. While the forward reactions are fast and inherently exothermic owing to the lower zero-point energy content of the products, the reverse processes have T thresholds. The results confirm their prominence in the overall interstellar C fractionation chemistry; the calculated rate constants can then be readily introduced in astrochemical reaction networks.

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Estudo Teórico da Formação de Glicolaldeído no Meio Interestelar

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Palavras-Chave: Glicolaldeído, prebiótica, Interestelar.

Introdução

Na astroquímica, o glicolaldeído faz parte de uma classe de moléculas chamadas COM (Complex Organic Molecules), bem como o formaldeído e o etilenoglicol. Esta molécula já foi reportada em diversas regiões do espaço, desde nuvens moleculares frias (10K), até regiões de formação estelar com temperaturas mais elevadas e cometas, como o C/2014 Q2 (*Lovejoy*)¹.

Somada à sua ubiquidade em várias regiões do espaço, o glicolaldeído é um importante precursor de moléculas que são fundamentais para o aparecimento da vida, como açúcares, aminoácidos e material genético (ribose)².

Devido tanto ao seu potencial prebiótico quanto sua diversidade no universo, é altíssimo o interesse em saber o seu mecanismo de formação. Até então, os trabalhos teóricos e experimentais já realizados não definiram um caminho de formação do glicolaldeído no espaço, porém apontam que seu mecanismo de formação deve estar relacionado com reações catalisadas em superfície de gelo interestelar³.

Este trabalho tem como objetivo determinar, através de cálculos teóricos em fase gasosa e sólida, possíveis reações de formação do glicolaldeído, e assim ajudar a explicar a sua abundância no espaço.

Metodologia

Os cálculos em fase gasosa foram realizados a nível DFT, utilizando o funcional de troca-correlação M06-2X, com conjunto de base de Dunning aug-cc-pVQZ. Foram realizados cálculos de frequências vibracionais para confirmação das estruturas obtidas.

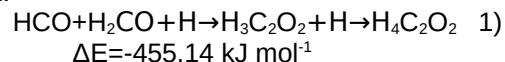
Cada estrutura de interesse obtida via DFT teve sua energia recalculada a nível CCSD(T) com resolução de identidade (RI) e correlação explícita (F12). O conjunto de base utilizado para este refinamento foi cc-pVQZ-F12.

Para simular reações em grãos, foi utilizado um programa próprio para gerar diversas células unitárias de gelo amorf, e através de uma análise energética foram escolhidas as 5 de menor energia. Em cada uma delas foram realizados cálculos DFT com condições periódicas e ondas planas com energia de corte em 40 Ry. A malha de pontos \mathbf{k} foi 2x2x2 para o *bulk* e 2x2x1 para as superfícies.

Definido o caminho de reação em fase gasosa, o mesmo foi testado na superfície de cinco gelos amorfos diferentes, através de mecanismo de reação Eley-Rideal (ER), difusão através da superfície, e Langmuir–Hinshelwood (LH), choque direto com a molécula suportada.

Resultados

Dentre os caminhos de reação testados, o que obteve menor barreira energética para a formação do glicolaldeído, foi através da reação entre formaldeído (H_2CO) e a molécula HCO, equação 1.



Onde $\text{H}_3\text{C}_2\text{O}_2$ representa o glicolaldeído desprotonado. A energia de ativação prevista para esse processo foi 27,7 kJ mol^{-1} , que é suficiente para inviabilizar reações em fase gasosa para a formação do glicolaldeído no espaço interestelar.

Em fase sólida, o mecanismo ER mostrou que a barreira energética prevista em fase gasosa não existe em nenhuma das superfícies pesquisadas. A reação 1 se torna uma reação sem energia de ativação quando realizada suportada por gelo. No mecanismo LH, foi constatado o mesmo comportamento da ER, na qual a molécula de HCO, proveniente do vácuo, forma a ligação carbono-carbono com a molécula de H_2CO suportada em gelo amorf, sem barreira energética.

Conclusões

Este trabalho sugere como o glicolaldeído pode ser formado sem barreira energética na superfície de um gelo interestelar. Desta forma, ajuda a explicar como essa molécula pode ser formada em nuvens moleculares frias do espaço e a importância das reações em superfície para a astroquímica.

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Agradecimentos

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Fine-Tuning the Polarizable CL&Pol Force Field for Molecular Dynamics Simulations of Ethaline Deep Eutectic Solvent

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Palavras-Chave: Solventes Eutéticos Profundos, Campo de Força Polarizável, Dinâmica Molecular

Deep eutectic solvents¹ (DESs) are an interesting class of materials resembling ionic liquids (ILs) systems with great potential applications in synthesis, electrochemistry, separation processes, and biomass transformation. DESs are mixtures of two or more substances, with at least one being a hydrogen bond donor (HBD) molecule and one being a hydrogen bond acceptor (HBA) molecule.

Traditionally, molecular dynamics (MD) simulations of DESs have been performed² with non-polarizable molecular mechanics force fields due to the computational cost and the lack of suitable polarizable force fields. Those simulations are mainly done with reduced charge models to account for electronic polarizability in a implicit way, similarly as done when simulating ILs³.

Recently, the CLPol force field⁴ became available, in principle, a general transferable polarizable force field (based on Drude oscillators) alternative to simulate DESs. However, the current set of parameters together with the force field specifications (“naked” hydrogens, diameter modification of the Lennard-Jones sites, chloride overpolarization, Tang-Toennis damping functions, and so on) results in phase separation when simulating the DES ethaline (choline chloride and ethyleneglycol mixture in 1:2 molar ratio). In this work, we fine-tune the parameters and correct the chloride overpolarization to direct the system in the right track. Then, we characterize the hydrogen bond network and structural correlations of the system and a comparison is made against experimental data and with the non-polarizable reduced charge version of the force field.

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Estudo da estrutura tridimensional de peptídeos zíperes de triptofano através de cálculos de deslocamentos químicos de ^1H e simulações de Dinâmica Molecular

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Palavras-Chave: Dinâmica Molecular, proteínas, Ressonância Magnética Nuclear.

Introdução

As principais funções biológicas das proteínas são decorrentes de suas estruturas primárias e, codificadas por essas, das conformações espaciais que assumem em solução. Atualmente, são utilizados diversos métodos, combinados ou não, para a determinação estrutural de proteínas. No entanto, estas metodologias possuem limitações, que podem tornar a determinação estrutural de proteínas um processo árduo e custoso.¹ Neste cenário, as ferramentas computacionais são uma ferramenta potencial no auxílio às técnicas experimentais.

Dessa forma, o objetivo deste trabalho é analisar, através de uma combinação de cálculos quânticos de deslocamentos químicos de ^1H e simulações de Dinâmica Molecular, as estruturas tridimensionais de peptídeos zíperes de triptofano (Trpzip).

Metodologia

O Trpzip1 (PDB ID: 1LE0) foi o primeiro peptídeo zíper de triptofano sintetizado.² Sua estrutura primária é constituída por uma sequência de 12 aminoácidos. Já a estrutura tridimensional é caracterizada por uma folha- β , com duas fitas antiparalelas unidas por uma volta- β , formando uma conformação β -hairpin. O Trpzip1 foi submetido a simulações de Dinâmica Molecular, utilizando o campo de forças CHARMM27, no software GROMACS. A partir desta simulação, foram selecionados 10 snapshots, que tiveram suas geometrias otimizadas em HF/3-21G, e seus deslocamentos químicos de ^1H calculados em GIAO-B3LYP/6-31G*. Todos os cálculos foram realizados utilizando método QM/MM, com a interface CHEMSHELL no software Gaussian 09.

Para analisar a estabilidade dos elementos de estrutura tridimensional dos zíperes de triptofano frente a alterações na sequência primária, foi proposto um peptídeo com uma mutação na região correspondente à volta- β do Trpzip1. O peptídeo mutante também foi submetido a simulações de Dinâmica Molecular e cálculos de deslocamentos químicos de ^1H .

Resultados e discussão

A partir de uma comparação das diferenças dos deslocamentos químicos de $^1\text{H}^\alpha$ do peptídeo mutante e do Trpzip1 em relação a valores de *random coil*

(figura 1), é possível observar que os dois peptídeos possuem padrões diferentes somente em relação aos deslocamentos químicos dos resíduos 5, 7 e 8, que correspondem à região de volta- β . Isto indica que ambos apresentam enovelamentos semelhantes nas regiões de fitas- β , porém tipos distintos de voltas- β .

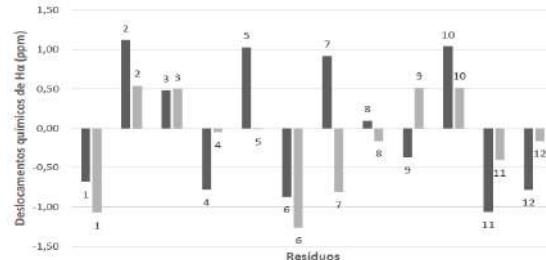


Figura 1. Diferenças nos deslocamentos químicos (em ppm) de $^1\text{H}^\alpha$ da estrutura calculada para o peptídeo mutante e o Trpzip1, em relação aos valores de *random coil*.

Ao ser sintetizada pela primeira vez, a estrutura do Trpzip1 foi caracterizada por uma volta- β do tipo pD.² Assim, foi usado o programa BetaTurnTool¹⁸³ para identificar os tipos mais prováveis de volta- β no peptídeo mutante e no Trpzip1.

Para o Trpzip1, foi assinalada uma volta- β semelhante aos tipos dD e dN. Este é um indicativo de que, possivelmente, a classificação dada anteriormente está incorreta. Por outro lado, o peptídeo mutante possui uma volta- β do tipo pD, que foi originalmente atribuída ao Trpzip1.

Conclusões

A partir dos cálculos e simulações realizadas, foi possível concluir que a classificação de volta- β que fora dada na literatura para o Trpzip1 está incorreta. Por outro lado, o peptídeo mutante proposto possui o tipo de volta- β determinada anteriormente para o Trpzip1.

Ademais, o protocolo de cálculos utilizado neste trabalho se mostrou uma ferramenta de baixo custo e com grande potencial para a análise de estruturas tridimensionais de peptídeos.

Agradecimentos

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Water Adsorption on Pt (100) and (110) surfaces: A Molecular Dynamics Study

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Palavras-Chave: Molecular Dynamics, Platinum Surface, Water.

Introduction Water is a cheap and non-toxic solvent, capable of solubilizing different solutes and is consequently, used in several chemical processes. An interesting subject involving water is its interaction with metal surfaces^{1,2}. Understanding this interaction has an important role in electrochemical reactions, corrosion, fuel cell reaction and photocatalysis². This study presents a molecular dynamics study of water adsorption on two types of platinum surfaces (100 and 110) varying the parameter ϵ_0 of the Lennard-Jones potential used to represents the platinum atoms.

Methodology Two boxes were created using Packmol³ each with 28961 molecules of water and one of the surfaces. The MD simulations were performed under NVT conditions at 298 K for 3 ns to minimization and equilibration, and a production step varying between 5 and 30 ns. Furthermore, we evaluated 22 values for the parameter ϵ_0 ranging from 0.80 to 9.80 kcal.mol⁻¹. The software NAMD⁴ was used for all simulations.

For a better visualization of the graphics, the results of only six values of ϵ_0 will be presented.

Results and Discussion The mean density of water molecules as function of the distance away from the surface was measured for Pt (100) (Figure 1A) and Pt (110) (Figure 1B) surfaces.

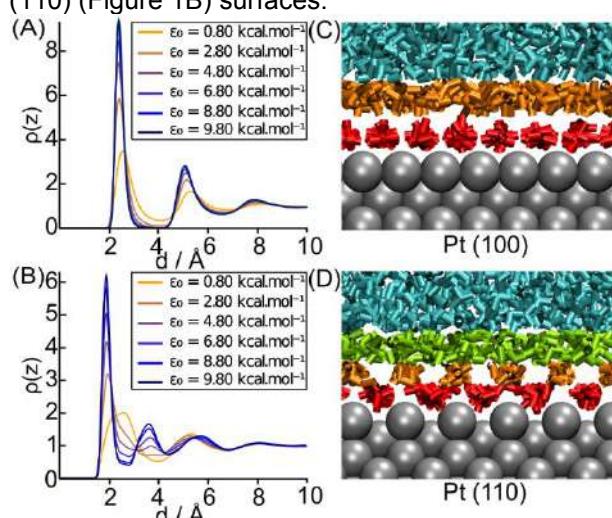


Figure 1. Structure and solvation of the water-metal interface. (A and B) The density profile of water molecules away from Pt (100) and Pt (110) surfaces respectively, divided by the bulk water density. (C and D) Typical configuration of water molecules, observed from the $\epsilon_0 = 4.80 \text{ kcal.mol}^{-1}$ for the 110 surface. In these figures, the 1st,

2nd and 3rd layers of water are represented by red, orange and green colors, and the bulk by cyan.

The water molecules on the first layer of Pt (100) surface form a hydrophobic network (Figure 1C). This is by the fact that hydrogen bonds formed in this layer are parallel to the surface, whereas on the 110 surface, the hydrogen bonds formed between the water molecules from 1st and 2nd layers have a puckered shape (Figure 1D).

In addition, the intermittent time-correlation function was calculated. It can be interpreted as the probability that a water molecule adsorbed at the time t still or again adsorbed at a time $t + \Delta t$ and the results are show in Figure 2.

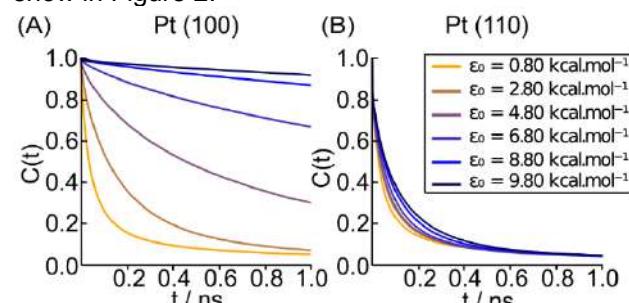


Figure 2. Intermittent time-correlation function calculated for 6 different values of ϵ_0 . (A) For Pt (100) surface. (B) For the Pt (110) surface.

Despite the different values for ϵ_0 , Figure 2 shows in general that the residence time of a water molecule on the (100) surface is longer than on the (110). This difference is probably caused by the proximity of the 1st and 2nd water layers on the (110) surface, and the shape of the hydrogen bonds, which provides higher mobility of the water molecules.

Conclusion The results indicate that the lower packing of the Pt (110) surface enables water molecules to adsorb and desorb faster than molecules on (100) surface. Moreover, the variation of the parameter ϵ_0 seems to have a small influence in the case of Pt (110).

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QTAIM analysis of the [4+2] Diels-Alder intrinsic reaction coordinate

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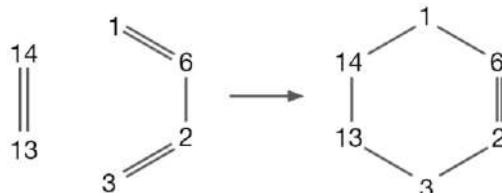
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Keywords: *Diels-Alder, QTAIM, electron density*

INTRODUCTION

The Diels-Alder reaction mechanism has been extensively studied by chemists both experimentally and theoretically since its first description, with a solid basis on MO theory and the Woodward-Hoffman rules. It consists of a reaction between a conjugated diene and a substituted alkene in order to form a cyclohexene derivative [1].



Diels-Alder reaction between 1,3-butadiene and ethylene. The carbon atoms are enumerated coherently to the results section.

During the 1960's, a new approach to chemistry was first developed by Richard F. W. Bader. This new approach uses the electron density rather than molecular orbitals as the source of information in chemical analysis, defining an atom as a region bounded by surfaces in which electron density flux is zero, therefore named as QTAIM – Quantum Theory of Atoms in Molecules [2].

The present work aims to investigate how some QTAIM-related properties in specific bond critical points (BCP) change along the intrinsic reaction coordinate steps.

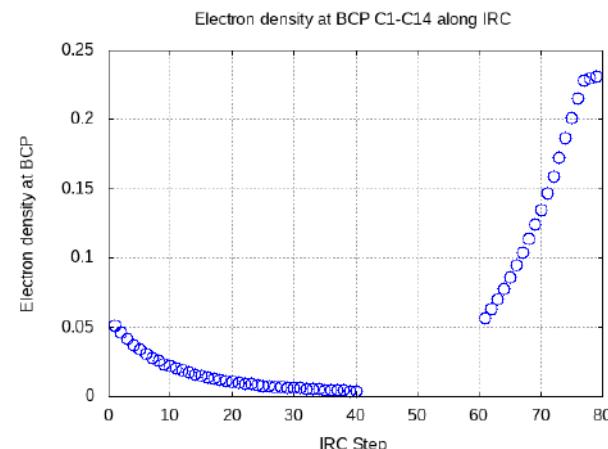
METHODOLOGY

A geometry optimization of the 1,3-butadiene + ethene reaction transition state was performed using the software Gaussian16 (B3LYP/6-311G**). Using the same method and basis set, its frequencies were calculated in order to verify if the geometry was indeed a saddle point in the potential energy surface, which was verified to be true due to the existence of a single imaginary frequency with a vibration mode coherent to the reaction.

Subsequently, the intrinsic reaction coordinate was calculated, resulting in 80 steps, in which an electron density profile was calculated for each of them. From these results, a QTAIM analysis for each step was performed using the software AIMAll.

RESULTS

The electron density in the BCP between carbon 1 and 14 curiously decreases, as shown in the graph below. Due to the vertical symmetry of the system, these values are the same for the BCP between carbon 3 and 13 up to the third decimal place. From the IRC steps 43 to 62, this BCP has vanished.



CONCLUSIONS

The results are coherent to previous literature about the vanishing of BCPs and their existence despite the presence of a chemical bond [3]. This is an on-going project aiming to further QTAIM studies of organic reactions under different methods and basis sets.

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ACKNOWLEDGEMENTS

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Identification of B Cell Epitopes and Disordered Regions of *Plasmodium falciparum* Apical Membrane Antigen 1 (PfAMA1)

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Palavras-Chave: AMA1, Epitopes Prediction, Intrinsically Disordered Proteins.

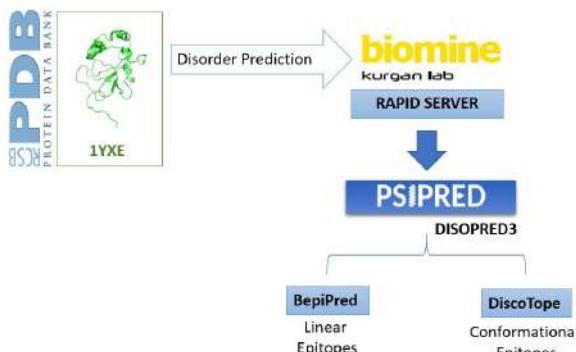
INTRODUCTION

Plasmodium falciparum, the etiological agent responsible for most deaths and severe cases of malaria, has a proteome marked by many intrinsically disordered regions (IDRs) and highly polymorphic proteins. These factors make malaria a challenge for the development of effective drugs and vaccines. Feng and co-workers⁽¹⁾ obtained the AMA1 protein crystallographic structure by NMR, which is a promising target, acting at two stages in the disease life cycle and in the notorious moving junction that is closely related to the invasion of host cells by the parasite. Since polymorphism and intrinsic disorder are related to the ability of the antigen to overcome the selectivity of antibodies, and epitope mapping indicates the regions of interest of its interaction, analysis of regions of disorder and epitope prediction are useful and essential for vaccine development and understanding immune activity.

METHODS

This work performed the disorder regions prediction of the PfAMA1 domain II and, subsequently, the linear and conformational epitopes, regions of high importance for antigen-antibody interaction, as shown in Figure 1.

Figure 1. Methods used for epitope prediction and intrinsic disorder of AMA1.

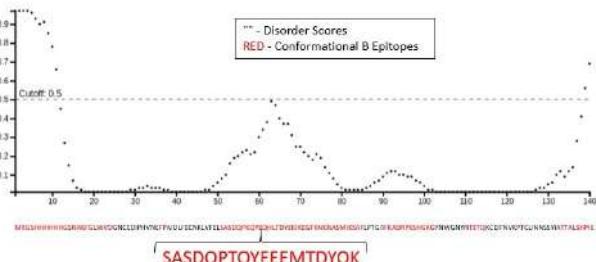


RESULTS

PfAMA1 has three known domains and about 20% intrinsic disorders. Through the RAPID server⁽²⁾, it was possible to observe that domain II is responsible for 7.14% of the disorders, being

considered a more structured protein than the others observed in this species. The disorder scores obtained by DISOPRED3⁽³⁾ can be seen in Figure 2. The amino acid sequence compared to the graph shows the conformational epitopes predicted by DiscoTope⁽⁴⁾ in red and, in the sequence below, we can observe that epitopes are found in the most disordered regions of the protein, which may have a strong relationship with the difficulty in developing effective vaccines and the ability of the pathogen in overcoming antibody selectivity. The highlighted sequence SASDQPTQYEEEMTDYQK has already been reported as an epitope in other studies⁽⁵⁾ in different *Plasmodium* species, indicating that this is a conserved disordered region that is important for antigen-antibody interaction.

Figure 2. Predicted epitope amino acid sequences in red are related to disorder score regions.



CONCLUSIONS

For an effective vaccine, it is necessary to trigger a strong humoral B-cell response. Thus, locating and mapping epitopes is essential to choose peptides with vaccine potential and understand the regions of protein disorder that are related to diseases.

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Estudo Teórico das Propriedades Estruturais e Eletrônicas da Molécula do Xanthohumol usando a Teoria do Funcional da Densidade (DFT).

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Palavras-Chave: *xanthohumol, propriedades eletrônicas, DFT*.

INTRODUÇÃO

O Xanthohumol é uma chalcona prenilada (flavonoide), sendo encontrado em abundância nas glândulas de lupulina do lúpulo. Nos últimos anos, diversos estudos têm mostrado que essa molécula, além de outras chalconas, apresenta atividade farmacológica que auxilia no combate de diversos tipos de câncer tais como: o de próstata, o de mama, o de cólon do útero e o de ovário. Outros estudos sugerem a atividade anti-HIV-1¹. Nesse contexto, o presente trabalho propõe a aplicação do método da Teoria do Funcional da Densidade para estudar as propriedades estruturais e eletrônicas dessa molécula.

METODOLOGIA

Nesse trabalho, todos os cálculos foram realizados usando o software ORCA, versão 4.1.1², para Windows 64 bits. Inicialmente, foi realizada a otimização da geometria da molécula de interesse. Após a confirmação de que a mesma era um mínimo de energia, foram realizados cálculos das propriedades eletrônicas de interesse nesse estudo tais como: (i) modos vibracionais; (ii) mapa de potencial eletrostático; (ii) morfologia dos orbitais HOMO/LUMO e (iii) análise eletrônica populacional, usando o modelo de Hirshfeld. Todas as propriedades acima foram calculadas considerando o nível da teoria do DFT/ B3LYP e o conjunto de bases 6-31+G(d,p), sendo utilizado, em todos os casos, a água como solvente, considerado o modelo CPCM.

RESULTADOS E DISCUSSÃO

A ausência de frequências imaginárias nos modos de vibração molecular indicou que a estrutura otimizada era verdadeiramente um mínimo de energia. Além disso, o espectro vibracional calculado apresentou diversas bandas características dos grupos funcionais presentes na molécula, os quais apresentaram correlação com os valores observados experimentalmente. O mapa do potencial eletrostático, assim como a análise populacional revelaram, de forma significativa, que a molécula apresenta regiões suscetíveis a ataques eletrofílicos e nucleofílicos, sendo que a densidade eletrônica era maior nos átomos de oxigênio dos grupos carbonila, hidroxila, além dos átomos de carbono nos sistemas aromáticos, respectivamente.

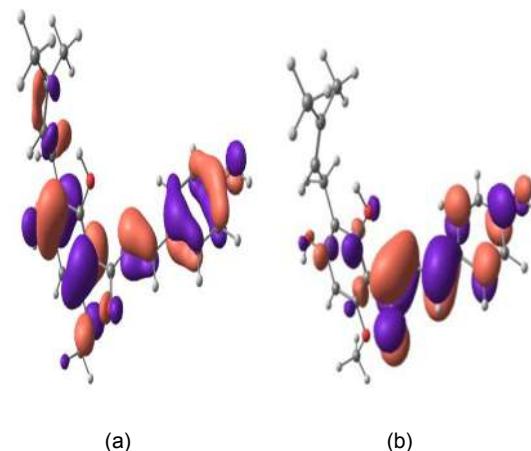


Figura 1. Morfologia dos orbitais (a) HOMO e (b) LUMO.

Por outro lado, notou-se que tanto os átomos de hidrogênio, quanto os de carbono, ligados aos grupos hidroxila, apresentaram déficit eletrônico devido à eletronegatividade do átomo de oxigênio. A Figura 1 apresenta a morfologia dos orbitais HOMO/LUMO do xanthohumol, os resultados indicam que a densidade eletrônica do orbital HOMO está significativamente dispersa sobre a superfície molecular, sendo predominante nas regiões com maior densidade eletrônica (ligações duplas, duplas conjugadas e nos grupos contendo oxigênio). Entretanto, percebe-se que o orbital LUMO está menos deslocalizado, indicando que é mais suscetível a ocorrência de ataques nucleofílicos na região central e aromática em que se alocam os átomos de carbono da molécula.

CONCLUSÕES

Os resultados mostraram que o método DFT foi adequado à obtenção de propriedades eletrônicas e estruturais do xanthohumol. A elucidação das propriedades de moléculas com aplicação farmacológica consolidada ou potenciais candidatas e de extrema importância para o desenvolvimento e o planejamento racional de novos fármacos ou formulações com potencial aplicação médica.

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Sarin-air mixture filtration by a porous rGO: a molecular dynamics study

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Keywords: Sarin, graphene oxide, filtration.

Introduction

Sarin is an organophosphorus compound, known to be one of the most dangerous chemical warfare agents due to its action on acetylcholinesterase enzyme, lethally affecting the muscles performance [1]. Literature presents several works about sarin detection, however only few ones on its filtration. In particular, few works explored the possibility to use nanostructures to filter sarin. In this work, classical molecular dynamics (MD) simulations are carried out to investigate the filtration process of sarin gas from a sarin-air mixture by porous reduced graphene oxide membranes (rGOs).

Methodology

A simulation box of $32.2 \text{ \AA} \times 34.2 \text{ \AA} \times 200 \text{ \AA}$ was created and a rGO membrane was placed in the middle, dividing the box in two regions. The origin of the z-coordinate is defined on the membrane. A mixture of sarin-air with different sarin concentrations (9%, 17% and 28%) was initially placed on one side of the box, leaving the other side empty. MD simulations of the air-sarin mixture were performed using the LAMMPS package [2] and Nose-Hoover thermostat at temperatures varying from 300 to 900 K, as done before in a study of filtering sarin by pure graphene [3]. Using a timestep value of 1 fs, simulations were run for a total amount of time of 10 ns

Results

Figure 1 shows the number of particles per volume along z direction for sarin (at a concentration of 17%) (a) and air (b) for different temperatures and for the system with one rGO nanosheet. They indicate that sarin has a strong tendency to surround the rGO nanosheet, evidenced by the peak in sarin density around $z = 0 \text{ \AA}$. Different from what happens between sarin and pure graphene [3], this concentration around rGO does not change much with the temperature. Fig. 1(b) shows that the air density also presents a similar behavior, although the flattening of

curves with the temperature increase indicates a less intense interaction between air and rGO compared to that between sarin and rGO.

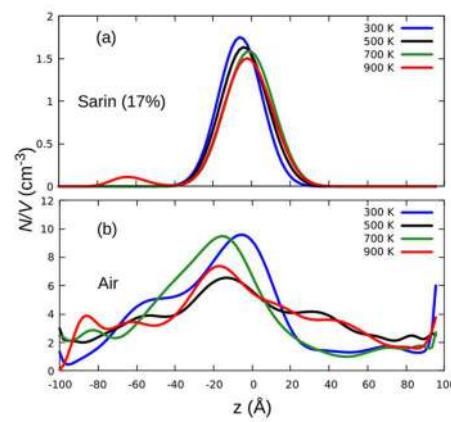


Figure 1. Particle density along z direction.

Conclusions

The results show that porous rGO nanosheets are able to allow the passage of the air blocking sarin molecules. Thus, it indicates that rGO membranes are good candidates to make good filters for sarin-air mixtures.

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Estudo Computacional de uma Reação Química Consecutiva com Formação de Intermediário Reacional usando o Método de Monte Carlo

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Palavras-Chave: Método de Monte Carlo, Intermediário reacional, Química computacional.

Introdução

O estudo teórico de diversos sistemas químicos possibilita uma melhor compreensão de resultados experimentais ou a extração de algumas condições laboratoriais de difícil controle e/ou reprodutibilidade. Nesta perspectiva, o Método de Monte Carlo (MMC) tem se mostrado uma ferramenta extremamente útil para o estudo cinético de diversos sistemas físico-químicos.¹ Neste trabalho, uma reação química consecutiva bimolecular, com formação de intermediário reacional, foi simulada usando-se o MMC e o Modelo de Urna de Ehrenfest (MUE). O mecanismo reacional está esquematizado nas Equações 1 e 2



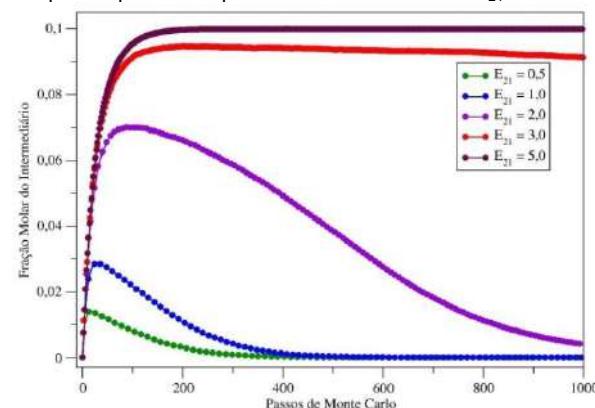
Modelo computacional

As equações $P_1 = e^{-\frac{1}{\theta}}$ e $P_2 = e^{-\frac{E_{21}}{\theta}}$ definem as probabilidades de ocorrência das reações elementares 1 e 2 respectivamente. Para isso, foram definidos os parâmetros adimensionais θ e E_{21} , sendo $\theta \equiv \frac{k_B T}{E_1}$ e $E_{21} = \frac{E_2}{E_1}$, onde k_B é a constante de Boltzmann e T a temperatura. E_1 e E_2 são respectivamente as energias de ativação para a primeira e a segunda reação elementar. A dinâmica da simulação é definida usando o MMC em conjunto com o MUE. Em cada passo computacional o MUE define as moléculas que colidem, enquanto que o MMC define as chances das moléculas reagirem a partir dessas colisões.

Resultados e Discussão

A Figura 1 mostra a fração molar da espécie intermediária ($X_{AB^{\#}}$) em função do tempo computacional. Os resultados das simulações mostraram que há um período de indução, na qual a espécie $AB^{\#}$ atinge um valor máximo de fração molar. Tal período de tempo independe da relação E_2/E_1 simulada. Por outro lado, foi observado que a espécie intermediária tende a apresentar um comportamento de estado quase estacionário ($\frac{dX_{AB^{\#}}}{dt} \approx 0$) à medida que a razão E_2/E_1 aumenta.

Figura 1 – Fração molar do intermediário reacional em função do tempo computacional para diferentes valores de E_{21}



O aumento do parâmetro E_{21} significa o aumento da energia de ativação da segunda etapa (E_2) em relação à energia de ativação da primeira etapa (E_1). Tal aumento acarreta em diminuição da taxa de consumo de $AB^{\#}$, pois serão menores as probabilidades de ocorrência da segunda reação elementar, uma vez que P_2 tende a assumir valores cada vez menores quando E_{21} tende a valores crescentes, acarretando em aumento no tempo de existência do intermediário reacional. Nos casos em que $E_2 = 3E_1$ (curva vermelha) e $E_2 = 5E_1$ (curva marrom) a espécie intermediária manteve-se com fração molar praticamente constante após atingir a fração molar máxima. Nestes casos, as reações da segunda etapa elementar só ocorrem ocasionalmente, devido a menor probabilidade P_2 , de modo a não consumir totalmente o intermediário formado, considerando o intervalo de tempo definido na simulação, caracterizando um estado quase estacionário em ambos os casos.

Conclusão

O algoritmo desenvolvido mostrou-se adequado à simulação do mecanismo de reação proposto neste trabalho. Observou-se que o parâmetro relacionado às energias de ativação da primeira e da segunda etapa, tem influência nos perfis reacionais obtidos.

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An integral grid-based variational method applied to vibrational spectroscopy

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Palavras-Chave: Schrödinger equation, Vibrational spectroscopy, Morse potential, Numerical methods.

1. INTRODUCTION

The integral grid-based variational (IGBV) method is being developed for some quantum problems in the last few years, such as harmonic oscillator¹, Hartree-Fock atomic energies², and confined multielectron atoms³. In this work, IGBV method is applied to anharmonic vibrational spectroscopy.

2. METHOD

The two-body vibrational Schrödinger equation in its integral form is written as:

$$E_{vib} = \frac{-\hbar^2}{2\mu} \int \psi^*(r) \frac{d^2\psi(r)}{dr^2} dr + \int \psi^*(r) \hat{V}(r) \psi(r) dr$$

where μ is the reduced mass of a diatomic molecule, E_{vib} is the vibrational energy associated to the potential energy operator, in this case, the Morse potential:

$$\hat{V}(r) = D_e \left(1 - e^{-\beta(r-R_e)}\right)^2$$

where D_e , R_e , and β are constants that depends on the molecular system. To solve Schrödinger equation, a discrete random wavefunction is generated with 50 points, and the vibrational energy is calculated by the numerical integration using the trapezoid rule. The numerical derivatives are calculated using the 7 points formulae. The discrete wave function points are randomly selected and modified to minimize the vibrational energy according to the variational principle.

The wavefunction of the excited states are obtained in a similar way but imposing the orthonormalization through the Schmidt method.¹⁻³

3. RESULTS AND DISCUSSION

Table 1 shows calculated and experimental energies of five vibrational states and some spectroscopic parameters for O₂ and Cl₂. As expected, the error of numerical energy increases with the level of the excited state, because they are generated one at a time and are orthonormalized with respect to all previous states, which increases the error for higher states. The spectroscopic parameters present a good accuracy and suggest

that a larger number of points should be used. However, the simplicity and excellent numerical behavior suggest that the method should be considered for determination of eigenvalues and eigenvectors of systems described by more complex potentials.

Table 1. Energies and spectroscopic parameters (in cm⁻¹) from IGBV and experimental of five vibrational states of O₂ and Cl₂ molecules.

Molecule	Parameter	IGBV (cm ⁻¹)	Experimental (cm ⁻¹)
O ₂	E ₀	785.9504	786.3808
	E ₁	2333.3618	2336.8741
	E ₂	3843.2813	3857.6760
	E ₃	5308.0925	5348.7867
	E ₄	6718.5828	6810.2061
	ω _e	1578.0812	1580.1930
	ω _e x _e	12.9920	11.981
	ω _e y _e	-1.3127	0.0475
	E ₀	278.8221	278.8962
	E ₁	830.2708	830.8940
Cl ₂	E ₂	1372.5493	1375.1657
	E ₃	1904.1603	1911.7115
	E ₄	2423.2900	2440.5313
	ω _e	559.3030	559.7200
	ω _e x _e	3.4644	2.675
	ω _e y _e	-0.2568	-0.0067

4. CONCLUSIONS

The IGBV method is numerically well-behaved for vibrational systems and should be considered as alternative for the calculation of vibrational eigenvalues and eigenvector for more complex systems. More efficient methods of optimization are being tested as well as other general conditions.

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Role of coulomb interactions and density on the viscosity and non-newtonian behavior of ionic liquids – a molecular dynamics study

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Palavras-Chave: *ionic liquids, non equilibrium molecular dynamics, rheology*

Ionic liquids (ILs) are defined as ionic compounds with melting point lower than 100°C. Due to their essentially null volatility, great thermal and chemical stability, good adhesion and large viscosity index, there is a great interest in using these compounds as lubricants and as lubricants additives.¹ The huge number of possible cation-anion combinations would, in principle, enable to fine tune the physical properties of an IL for a given application if their correlation with the chemical structure is known. In applications as lubricants, shear rates of the order of GHz can be produced even for small operation velocities if the liquid film has a thickness of nm scale. In these situations, ILs displays a shear thinning behavior (a reduction of the viscosity with shear rate) even if under the small rates studied in typical rheology experiments they show newtonian behavior. Hence, it is desirable to know not only how the intermolecular interactions determines the zero shear viscosity of an IL, but also how they modulate the shear thinning.

Non-equilibrium molecular dynamics (NEMD) simulations permits to impose a controlled shear rate and measure the resulting viscosity in ranges that are not accessible to typical experiments while also enabling detailed analyses of the liquid structure at the molecular level. In a previous work, we explore the effect of different anions and notice that some structural changes due to the shear rate can be fitted using Carreau equation and correlated to the shear thinning.² In the present work we aim at the role of electrostatic interactions and of density over the viscosity of ILs. In one hand, the intense electrostatic interactions in ILs are likely to give rise to their high viscosities. On the other hand, the high density of ILs can also contribute to the high viscosity, thus, a question remains of how much is due directly to the intense ion-ion interactions and how much is actually due to the high density.³

In order to tackle this question, we performed NEMD simulations of the 3-butyl-1-methyl-imidazolium tetrafluoroborate using the Martini 3.0 coarse grained force field with LAMMPS software. Four model systems were considered. The first uses the regular parameters of the force field, which uses a relative dielectric constant $\epsilon_r = 15$ to attenuate coulomb interactions. This first model, however, results in a zero shear viscosity much smaller than the one found in atomistic simulations with explicit polarizability (orange curve in Figure 1)

and on experimental works. A value of $\epsilon_r = 5$ (red curve) was found to give viscosity results very similar to the ones found in the atomistic model and was studied as the second model. In the third and fourth systems the electrostatic interactions were turned off, with only the dispersion forces described by Lennard Jones potential remaining. In one of them the liquid volume was allowed to relax under constant pressure (green curve), resulting in a smaller density than in the charged systems, while in the other (blue curve) the volume was held equal to the $\epsilon_r = 5$ system. Thus, in the last we have a pure description of the removal of ionic interactions. The largest effect over viscosity is confirmed to be directly due to coulomb interactions, while the change in density due to absence of them results in a further but smaller reduction. The coulomb interactions also are the main factor determining at which rate the shear thinning starts and this effect is correlated with changes in liquid structure.

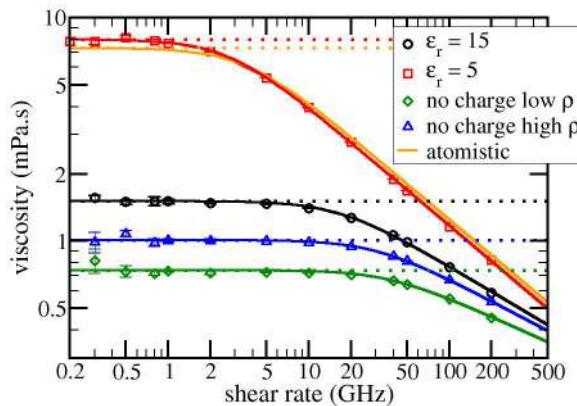


Figure 1 – Dependence of the viscosity with the shear rate in the studied model. Carreau equation fit is given by the solid lines. Dotted horizontal lines corresponds to the calculated zero shear viscosity.

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Analysis of the influence of conformational information in 3D-QSAR modeling

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Keywords: Conformational information, 3D-QSAR, molecular alignment.

Introduction

Multivariate Image Analysis applied to QSAR (MIA-QSAR) is a simple alignment-based QSAR approach based on the understanding that 2D chemical structure images contain relevant topochemical and topostructural information encoded in their elementary units, pixels.¹ Accordingly, in this technique, pixel values are used as molecular descriptors to correlate chemical structures with their respective response properties. Although it has proven to be an efficient approach to explaining a variety of properties of different molecule datasets, some criticisms have been raised based on the premise of the lack of conformational representation, necessary to explain the spatial requirement for ligand-enzyme fit-based bioactivity. In this sense, efforts for encoding spatial information into the technique have been performed; however, the results showed no improvements in the prediction capability of the models.² Therefore, we inquire whether conformational information is indeed an essential condition to obtain predictive and interpretable QSAR models. Accordingly, the goal of this study was to explore the dependence of 3D-QSAR modeling on spatial features through the use of different molecular representations, which vary from flat congruent structures to the most likely bioactive conformations.

Materials and Methods

Initially, a series of unsymmetrical aromatic disulfide compounds with anti-SARS-CoV (severe acute respiratory syndrome coronavirus) activity was selected from the literature.³ A first 3D-QSAR model (I) was obtained with molecules without any pre-treatment and the coincident substructures were perfectly congruent and planar, such as in a 2D representation. A second model (II) was generated based on molecules with quantum-chemically optimized structures (computed at the ω B97X-D/6-311G(d,p) level of theory using the Gaussian software), with the goal of obtaining the most stable conformations. Lastly, a model (III) was built using the most likely bioactive conformations obtained after docking the chemical structures into the M^{pro} (main protease) enzyme (PDB code: 2AMD) with the aid of the Glide ligand-receptor docking tool. All 3D-QSAR models were built using the Open3DQSAR tool. Steric and electrostatic fields were computed using a carbon atom probe and a volume-less probe with +1 charge. A variable selection procedure was carried out in order to remove the less influent variables

during the construction of each model. The robustness of the models was evaluated based on the following statistical parameters: r^2 , q^2 , and r^2_{pred} . To facilitate the comparison among the models, a scoring parameter was added, which consists of a simple arithmetic average of the validation parameters.

Results and Discussion

Table 1 shows the statistical parameters obtained for each approach. The results are for a 1.5 Å step size box surrounding all molecules and leaving 4.0 Å outgap around the largest.

Table 1. Statistical validation parameters for the 3D-QSAR models.

Model	LV	r^2	q^2	r^2_{pred}	Score
I	2	0.824	0.670	0.891	0.793
II	3	0.913	0.721	0.792	0.807
III	2	0.773	0.434	0.438	0.547

Considering the scoring parameter above, one can notice that the models built with flat molecules (I) and fully optimized structures (II) were very similar in terms of predictability. On the other hand, the approximation of the chemical structures to their most likely bioactive conformation (III) seems to have compromised the quality of the validation parameters. Therefore, the robustness of the models seems to be more related to the alignment aspect of the structures than to how well their tridimensional aspects are described. As a future perspective, the authors intend to analyze the impact of the different molecular representations on the interpretability of these models comparing their steric and electrostatic molecular fields.

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An ONIOM approach for calculating the UV-Vis spectra of warfarin

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Palavras-Chave: TD-DFT, ONIOM, UV-Vis

Introduction Multi-scale and hybrid methods, commonly ONIOM (Our N-layered Integrates molecular Orbital Mechanics)¹, are strategies frequently used to reduce computational costs and employed to calculate electronic properties of large molecular systems. The approach considers the system into different regions. The “core” of the system (model) is treated at higher level of theory while the rest of the system (real) is treated at less computationally demanding level. The ONIOM main feature is that the energy of the system is a extrapolation of the energy calculated for the real and the model systems. Besides, it can be expandable for three or more layers obtained independently, if no electronic embedding schemes are employed. Methods based on ONIOM for extrapolation of absorption spectra with hybrid QM/QM method were reported.² In this work we propose the use of ONIOM approach in the theoretical calculation of UV-Vis spectra of the warfarin.

Methodology All calculations were performed with GAUSSIAN16.³ All the geometries were optimized at B3LYP/6-311++G(2d,p) level of theory. For the target spectra, was used PBE0/6-311++G(3df,2p) level of theory in the TD-DFT considering the first 15 excited electronic states. For the lower level of theory was used the same functional but four different basis sets: 6-311++G(3df,2p) (as reference), 6-31++G(2df, p), 6-31G(2d,p) and 6-31G(d). The effect of implicit solvent was evaluated using PCM (ONIOM-PCM-x)⁴ and SMD models. It was added a third layer of explicit solvent molecules at HF/6-31G(d) level of theory.

Results The target spectra showed a maximum wavelength (λ_{tar}) of 287.51 nm, in good agreement with experimental result ($\lambda_{exp}=307$ nm).⁵ The maximum of absorption can be associated with HOMO→LUMO electronic transition. The frontier molecular orbitals are mostly localized at the aromatic double rings, and this region was defined as the “model” subsystem for the two layers ONIOM calculations. The results are shown in Table 1.

Table1. Maximum wavelength for ONIOM calculations in two layers.

Id.	Model	Real	$\lambda_{max}(\text{nm})$
1	6-311++G(3df,2p)	287.5	
2	6-31++G(2df,p)	287.7	
3	6-311++G(3df,2p)	6-31+G(2d,p)	287.7
4		6-31G(2d,p)	288.9
5		6-31G(d)	289.0

The Id. 1 shows that, when both subsystems are calculated at the same level of theory, the λ_{max}

observed is equivalent to λ_{tar} . When the basis set for the “real” subsystem is decreased, it is observed a variation in 1,3 nm of the λ_{max} , which is compensated by the gain in computational efficiency. For example, in spectra calculation without ONIOM are used 1,526 basis functions and 1,195 primitives. In Id.5 are employed 708 functions and 377 primitives. When added the effect of implicit solvent, the results were improved and the variation was smaller (1.0 nm for PCM and 0.9 nm SMD), as shown in Table 2.

Table 2. Maximum wavelength for ONIOM in two layers and implicit solvent models

Id.	1	2	3	4	5	$\lambda_{tar}(\text{nm})$
PCM	288.8	288.9	289.0	289.7	289.8	288.8
SMD	289.0	289.2	289.2	289.8	289.9	289.0

The structure containing a warfarin molecule inside a cube and water molecules located at vertices of this cube was fully optimized. This new layer was considered as the lower level (HF/6-31(d)), except for Id.0, where the three layers were described in the highest level of theory. The other two layers were kept the same as before. Results are shown in Table 3.

Table3. Maximum wavelength for ONIOM calculations in three layers.

Id.	0	1	2	3	4	5	λ_{tar}
λ_{max} (nm)	284.7	283.7	283.8	284.1	284.9	285.3	284.1

A small deviation has been observed in comparison to the λ_{tar} (without ONIOM) and λ_{max} of the Id.0 calculation. Even when comparing Id.5 (the smallest level used) with λ_{tar} , the deviations is about only 1.2 nm.

Conclusions ONIOM can be a useful tool to asses UV-Vis spectra with a gain in efficiency without losing accuracy. A variation as small as 1.2 nm in comparison with a significant decreasing in computational costs were observed. Another point to be explored is the large number of combinations with QM/QM approach, according the needs and availability.

Acknowledgments The authors would like to thank CAPES (grant 88887.479840/2020-00), CNPq, FAPESP (grant no. 2013/08293-7) and the CCES-CEPID/UNICAMP for computational facilities.

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A numerical-variational solution of the Schrödinger equation for H₂⁺

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Keywords: Molecular hydrogen ion; Schrödinger equation; Numerical methods.

Introduction

A numerical method referred to as Fixed-Grid Variational (FGV) method was developed to solve the Schrödinger equation combining procedures based on the variation principle [1], and an integral numerical alternative to circumvent a curvilinear coordinate problem which has no explicit boundary conditions [2].

Once extended the possibility of applying FGV to any system of curvilinear coordinates, it is the objective of this work, to test the method to the hydrogen molecular ion.

The Fixed-Grid Variational Method

The FGV method combines numerical techniques of differentiation and integration to solve the Schrödinger equation in its integral form. The calculation initiates with a discrete arbitrary wave function represented by a mesh grid where each point is optimized to minimize the energy of the system according to the variational principle.

The Schrödinger equation for the H₂⁺ ion using the Born-Oppenheimer approximation is completely separable in spheroidal prolate coordinate system (ξ, η, ϕ), although it generates coupled equations. However, there are no explicit boundary conditions at the ends of the η coordinate domain and at the origin of the ξ coordinate. Therefore, a pseudo boundary conditions are created to allow the numerical solution.

Numerical Results

Simulations were carried out for wave functions, in each of the coordinates, with a number of points between 20 and 1000 points, varying by ten. The convergence limit for the wave functions was of 10⁻⁸ [1]. The best energy was then obtained by extrapolation to an infinite number of points. Excited states were generated by imposing the orthogonalization condition with respect to all lower states using Gram-Schmidt method.

Calculations were performed for nuclear separations between 1.0 to 5.0 a.u. **Figure 1** shows the electronic energy for three lowest sigma energy states.

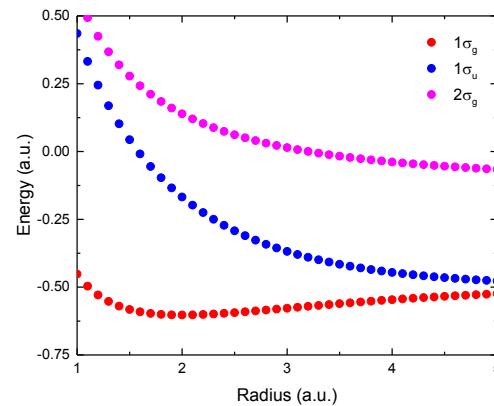


Figure 1. Energies, in atomic units, for states of the molecular hydrogen ion, found using the FGV method.

The results obtained have a mean absolute difference, with the results of the literature, of 9 · 10⁻⁶ a.u.. These values indicate the effectiveness of FGV and its applicability regardless of the curvilinear coordinate system used. In addition, the method simplifies the difficulties encountered, until today, in analytical solutions of this problem.

Conclusions

The extension developed to apply the FGV method to solve the Schrödinger equation in any curvilinear coordinate system, providing explicit boundary conditions, proved to be efficient in solving the molecular hydrogen ion problem, obtaining results with microhartree accuracy. Furthermore, the pseudo-boundary conditions proved to be efficient to produce the accurate numerical wave functions. These results suggest that the FGV method can be successfully applied to similar systems which present the same level of difficulty.

Acknowledgements

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Chemical bonding involving d-block elements from the quantum interference perspective

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Palavras-Chave: Chemical Bonding Theory, Transition Metals, Interference, Generalized Valence Bond.

Introduction

The nature of the chemical bond as a quantum interference phenomenon has been so far rigorously established for several classes of chemical bonds involving the main group elements.¹ The d-block elements, or transition metals, are often treated under the framework of the molecular orbital/ligand field theories, which numbs the connection with the conventional chemical bond concept in chemistry, and offers no explanation for the formation of chemical bonds in these compounds.

In order to obtain an unified view of chemical bond, we present preliminary results for coordinate bonds in the cation hydrides and chlorides of the first transition metal series of the Periodic Table, using the Generalized Product Function Energy Partitioning method (GPF-EP).² A GPF wave function is an antisymmetrized product of strongly orthogonal functions associated with groups of electrons of the molecule. According to the method, the total energy of the system can be split into two main terms, the interference and the quasi-classical components. We propose, as shown for the other cases previously studied, that the stability of the studied systems is dominated by the interference effect, and that the drop of the kinetic part of the interference energy is responsible of the stabilization of systems containing such bonds.

Methods

We considered the systems MH^+ and MCl^+ ($M = Ca-Zn$). The GPF wave function was constructed by treating the core orbitals at the HF level and the valence ones at the Generalized Valence Bond (GVB) level. The aug-cc-pVTZ basis was used. Potential energy surfaces were constructed for each species and the energy partitioning was performed at the global minima of the surfaces. The softwares GAMESS 2014 / VB2000 2.7 were used for the calculations.

Results

Figure 1 shows the total bond energy ($E[tot]$) partitioning of the studied species into the quasiclassical ($E[QC]$) and interference ($E[INT]$) terms, as well as the partitioning of the interference energy into its potential ($V[I]$) and kinetic ($T[I]$)

components. Quantum interference is clearly the major effect responsible for the formation of the chemical bond in all systems, the stabilization being provided by interference resulting from the drop in kinetical energy.

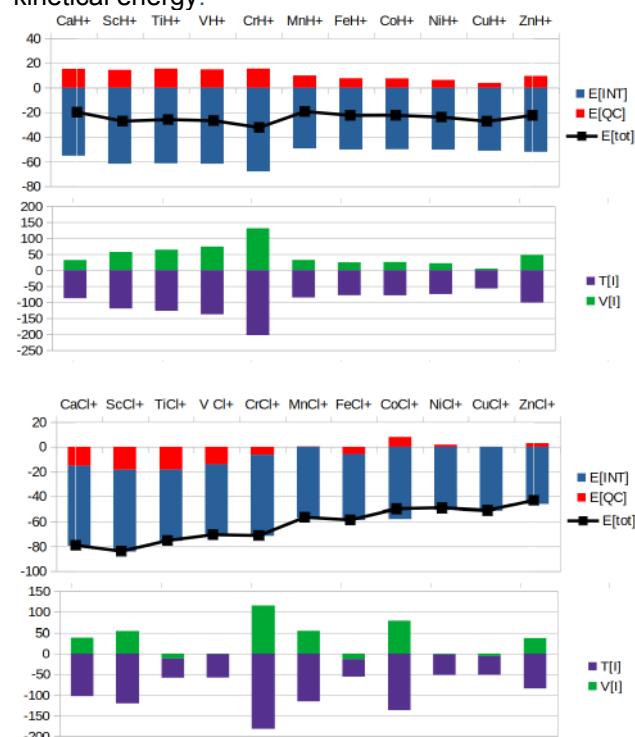


Figure 1. Total energy partitioning and interference energy partitioning for the MH^+ and MCl^+ species ($M = Ca-Zn$) at the GVB/aug-cc-pVTZ level.

Conclusions

The results of the GPF-EP analysis show that the ligand-metal bonds have the same mechanism of formation as a regular covalent bond. We soon hope to analyze and report results on more systems, particularly metal carbonyls and other complexes.

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Partial radial distribution functions for glassy GeSe₃ from scattering experimental data using the Hopfield Neural Network

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Palavras-Chave: *Partial radial distribution functions, scattering experimental data, Hopfield Neural Networks.*

Introduction

The radial distribution function, $g(r)$, plays an important role in the study of liquids and solids. Retrieving this function from the static structure factor, $S(k)$, obtained in scattering experiments is a common procedure.

Recently, the robustness of the Hopfield Neural Network (HNN) in inverting such experimental data was demonstrated for monoatomic liquids.[1,2,3] In this work, the HNN method will be applied to retrieve the partial radial distribution functions for glassy GeSe₃ from experimental data[4] to validate this methodology for solids as well. The performance of the HNN is to be analysed.

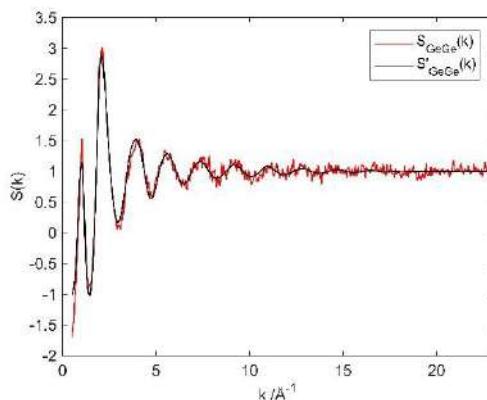


Figure 1 - Partial structure factor for Ge-Ge pair.

Methodology

Considering a linear transformation given by

$$\mathbf{s} = \mathbf{K}\mathbf{g}$$

in which \mathbf{s} is a vector of experimental data, \mathbf{K} is a transform matrix and \mathbf{g} is a vector to be determined. The linear HNN method consists in solving the following set of equations

$$\frac{d\mathbf{u}}{dt} = -\mathbf{K}^T \mathbf{K}\mathbf{g} + \mathbf{K}^T \mathbf{s}$$

with $g_i = g(u_i)$ called activation function and u_i the neuron state. The matrix \mathbf{K} relates to the Fourier transform at a given density, ρ :

$$S(q) - 1 = \frac{4\pi\rho}{q} \int r(g(r) - 1) \sin(qr) dr$$

Results

In Figure 1 it is represented the experimental data, $S_{GeGe}(k)$, and that retrieved in reference [4], $S'_{GeGe}(k)$.

The results for the radial distribution functions, $g_{GeGe}(r)$ acquired from experimental $S(k)$ and $g'_{GeGe}(r)$ from $S'(k)$, are presented in Figure 2 along with that obtained in reference [4].

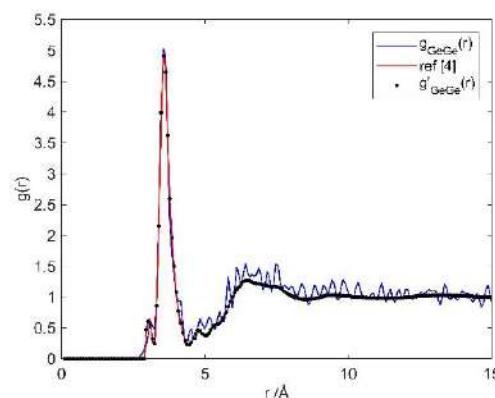


Figure 2 - Partial radial distribution function for Ge-Ge pair.

It was possible to accurately retrieve the radial distribution function from $S'_{GeGe}(k)$ with no need of auxiliary functions or any interpolation procedure. The results obtained from $S_{GeGe}(k)$ oscillates due the statistical errors present in the data, although the solution has the expected behaviour.

Conclusions

After this preliminary study it will be analysed the effect of smoothing the experimental results before applying the neural network and data with smaller noises, such as those for the pairs Ge-Se and Se-Se, will also be used to verify the performance of the HNN method.

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This work was supported by CNPq – Brazil.

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Structural and spectral evaluation of kratom (mitragynine)

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Keywords: Kratom; Infrared spectroscopy; DFT.

Introduction

The use of consciousness-altering substances has been reported throughout history. In recent decades, the use of synthetic substances has gained prominence due to their variety and quantity. However, due to uncertainty about the constituents of these drugs, compounds of natural origin were once again sought after. Thus, the main alkaloid extracted from the leaves of *Mitragyna speciosa* (Korth), mitragynine, was studied in this work [1]. The goal was to carry out the structural and infrared analysis of this structure using DFT and chemometrics. The idea is to verify if theoretical methods can help study illicit substances with forensic interest.

Methodology

A systematic conformational analysis was carried out using molecular mechanics in Avogadro software with the UFF force field to determine the possible conformers. The obtained structures were optimized in ORCA software using DFT PBE0/TZVP. Gibbs free energy was used to find the most likely conformer by May of the Boltzmann distribution, at 298.15K. With the global minimum structure, we evaluated the calculation parameters through a 2³ complete factorial design. We considered as factors: the DFT method (B3LYP and PBE0), the methodology for frequency calculation (Analytical and Numerical), and the use (or not) of correction for dispersion (D3BJ). The responses evaluated were computational time and RMSD. The analysis of this planning was performed with ANOVA and 95% confidence for the responses in the Chemoface software. We obtained eight theoretical infrared spectra from the factorial design. We compared them with the experimental ones obtained from the SWGDRUG database through Hierarchical Cluster Analysis (HCA). No pre-treatments were applied; the Euclidean distance and the incremental method were used as similarity conditions to form the clusters. In this step, the Pirouette software was used.[2]

Results

The systematic conformational analysis generated three possible structures. These were optimized in ORCA software using DFT B3LYP/TZVP. We observed that the differences among the conformers was around 1.9-2.6 kcal mol⁻¹. The conformer which presented the lowest Gibbs free energy showed a 94.7% probability of being observed according to the Boltzmann distribution. An RMSD of 0.436 was

obtained when comparing this conformer with the crystallographic structure. We used this structure for factorial planning. The responses indicated that the combination of B3LYP and analytical frequency was the most suitable one, once it was less time-consuming. The use of the D3BJ dispersion correction did not show to influence the evaluated parameters. HCA evaluation grouped the results for the theoretical infrared spectra by DFT, followed by methods for calculating frequency and using correction for dispersion. It is in accordance with findings observed through ANOVA. HCA results showed that the combination of B3LYP, analytical frequencies, and the correction for dispersion provided the greater similarity between theoretical and experimental spectra.

Conclusions

In this work, we used theoretical chemistry for studying compounds with forensic interests. We demonstrate that computational chemistry methods have great potential to obtain and improve the information about illicit substances. It can help to minimize errors in detection when there is no experimental information. Computations tools are important to study illicit drugs because they can be applied to circumvent regulatory restrictions. It is an advantage over experimental research. Besides, the procedure can be less costly and require less time to get answers when compared to benchtop experiments.

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Protein Solvation in ionic liquid mixtures

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Keywords: *Solvation, Proteins, Ionic liquid*

Introduction The study of biomolecules' behavior in electrolyte solutions is puzzling due to the huge variety of possible intermolecular interactions. Particularly, systems with biomolecules and ionic liquids (ILs) have been attracting interest because these compounds can interact in different ways with proteins.¹ In this work, we use minimum-distance distribution functions (MDDFs), Kirkwood-Buff integrals (KBIs), and time-correlation functions to understand the molecular basis of the ubiquitin solvation by electrolyte solutions of Ionic Liquids.^{2,7}

Methodology The simulation boxes were constructed using Packmol and the molecular dynamics (MD) simulations were performed using Gromacs.^{3,4} The simulated systems had 1.0 mol L⁻¹ solution of ionic liquids formed by the combination of the anions dicyanamide (DCA), nitrate (NO₃), and the cation 1-ethyl-3-methylimidazolium (EMIM). The systems discussed here are with solutions of EMIMDCA, EMIMNO₃ (systems with a solution of one IL), and EMIMDCA + EMIMNO₃ (system with a solution of a mixture of ILs). OPLS and OPLS-VSIL force fields were used for the protein and ILs, respectively.^{5,6} MD workflow is the same as previous work.⁷ The Analyses were performed using the packages [ComplexMixtures](#) and [ResTime](#).

Results and Discussion DCA and NO₃ show accumulation (Figures 1E and 1F) in the protein domain, with NO₃ having a KBI slightly greater than zero (Figure 1F). This means that these anions accumulate effectively in the protein domain, which indicates a favorable interaction with the protein. However, when the two anions are mixed (Figures 1A and 1D), DCA starts to display a higher accumulation in comparison with the system with just EMIMDCA, while NO₃ starts to be effectively excluded from the protein domain.

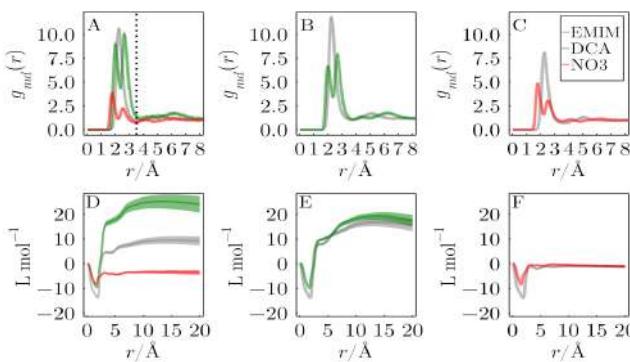


Figure 1 - Boxes from A to C display MDDFs for each system's components, while boxes from D to F display the KBIs. Peaks of MDDFs represent relative

accumulation according to the bulk concentration of the component being analyzed. The protein domain is up to 20 Å from the protein surface.

MDDF of DCA in EMIMDCA (Figure 1B) shows greater peaks than NO₃ in EMIMNO₃ (Figure 1C). In Figure 1A (EMIMDCA + EMIMNO₃), it can be noted that the MDDF peaks of DCA increase their relative height in comparison to Figure 1B. This means that DCA becomes relatively more concentrated around the protein in the mixture system with two ILs. The opposite can be noted for NO₃. A qualitative analysis of the time-correlation functions (Figure 2) suggests a higher residence time of DCA (in a region up to 3.5 Å from the protein surface, indicated by the vertical dotted line in Figure 1A) and a slightly smaller residence time of NO₃ in the systems with both in comparison with its corresponding systems with one IL.

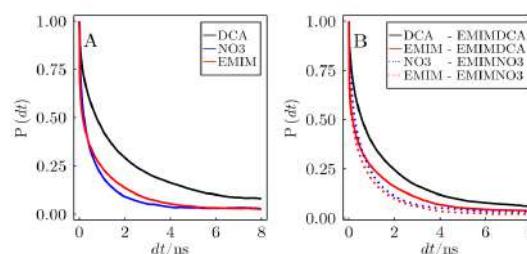


Figure 2 - Time-correlation functions for ionic species in systems with A) mixture of ILs and B) one IL.

Conclusions DCA displayed a greater interaction with Ubiquitin while NO₃ was relatively excluded when both were mixed. It seems that in systems with multiple electrolytes (like those studied here) the ion with a higher propensity to interact with the protein will dominate the interactions, while the ions with a smaller propensity to interact will be relatively exclusion.

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Out-of-plane IR intensities of $(B_6C)^{2-}$: a true challenge for DFT methods

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Palavras–Chave: $(B_6C)^{2-}$, IR intensities, out-of-plane.

In 2007, S. Shahbazian reported on the extreme sensitivity of $(B_6C)^{2-}$ system to the presence / absence of diffuse functions when modeling its out-of-plane vibration¹, a behavior mainly attributed to the floppy electronic density of this dianion and the high correlation energy between σ and π electrons¹. As infrared intensities are important descriptors of electronic density changes in molecules, it would be expected this molecule to show major differences on the intensities as well, in a similar fashion as reported by our group in various recent studies focused on out-of-plane vibrations. Considering that the original paper from Shahbazian reported solely on the $(B_6C)^{2-}$ IR frequencies, this abstract will be focused on the out-of-plane intensities of this system obtained from a number of different computational methods.

In view of the high sensitivity of the basis set, aug-cc-pVTZ was used in all calculations as originally advised.¹ Using Gaussian09, the $(B_6C)^{2-}$ structure was then optimized to a D_{6h} symmetry shape in various DFT (PBE1PBE, B3LYP, CAM-B3LYP, M05, M05–2X, M06–2X, M06–HF, MN15, B2PLYPD3, ω B97X–D and B97D3) and *ab initio* methods (HF, MP2, QCISD). Table 1 shows the more relevant data for the out-of-plane bending in this molecule.

Table 1. IR frequencies (cm^{-1}) and intensities (in $\text{km}\cdot\text{mol}^{-1}$) of the out-of-plane vibration of $(B_6C)^{2-}$.

Method	Frequency	Intensity
HF	330.65	925.39
PBE1PBE	318.03	1121.23
B3LYP	182.01	7323.63
CAM–B3LYP	342.99	503.46
M05	368.91	496.08
M05–2X	354.18	317.96
M06–2X	372.01	290.32
M06–HF	399.88	147.32
MN15	179.96	5978.64
B2PLYPD3	282.02	1770.84
WB97X–D	347.35	484.80
B97D3	394.76	4006.09
MP2	325.04	818.02
QCISD	332.43	487.73

One can see that the results from Table 1 indeed suggest a challenging situation. First of all, even though no imaginary frequency was found (probably due to the high quality of the basis set), there is a wide range between the lowest (179.96 cm^{-1}) and highest (394.76 cm^{-1}) frequencies. Interestingly, the two lowest frequencies are

delivered by one of the oldest (B3LYP) and newest (MN15) DFT methods tested. The results expected to be the most reliable ones, from MP2 and mainly QCISD, nicely agree to each other around 330 cm^{-1} .

The intensities show even larger differences. The weakest prediction ($147.32 \text{ km}\cdot\text{mol}^{-1}$) is only about 2% of the strongest one ($7323.63 \text{ km}\cdot\text{mol}^{-1}$), even though none of them seems to be a reliable prediction when looking the overall picture. Even the *ab initio* results show remarkable differences with MP2 predicting a band twice as strong than QCISD. Such dramatic differences do not fit the small differences on the bond lengths and atomic charges calculated from various models and reported in Table 2. All bond lengths are equal since the geometry has a D_{6h} symmetry.

Table 2. Bond lengths and atomic charges at carbon from the various DFT and ab initio methods for $(B_6C)^{2-}$.

Method	BL	$q_{C,CMS}$	$q_{C,Hirshf}$	$q_{C,CHELPG}$
HF	1.585	0.284	-0.070	1.311
PBE1PBE	1.588	0.275	-0.078	1.342
B3LYP	1.587	0.274	-0.078	1.467
CAM–B3LYP	1.578	0.285	-0.076	1.385
M05	1.591	0.262	-0.087	1.339
M05–2X	1.586	0.279	-0.075	1.238
M06–2X	1.585	0.277	-0.077	1.266
M06–HF	1.591	0.269	-0.080	1.093
MN15	1.585	0.271	-0.084	1.424
B2PLYPD3	1.596	0.268	-0.077	1.439
WB97X–D	1.588	0.272	-0.081	1.313
B97D3	1.601	0.263	-0.078	1.544
MP2	1.605	0.259	-0.079	1.413
QCISD	1.599	0.268	-0.075	1.304

As the equilibrium structures and atomic charges cannot be responsible for such large differences in the IR intensities, these must be caused by expressive changes in the charges (charge transfers) as well as in the atomic dipoles (since atomic charges themselves cannot correctly reproduce out-of-plane intensities). A complete CCTDP analysis is being carried out for this molecule right now and should be presented in full soon.

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Cálculos QM/MM ONIOM para a obtenção de informações sobre inibidores da toxina A da ricina (RTA)

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Palavras-Chave: RTA, QM/MM ONIOM, Energias de Ligação.

Introdução

A ricina é uma proteína citotóxica produzida na semente da mamona (*Ricinus communis*); pertence à família de proteínas inativadoras de ribossomos (tipo 2). Trata-se de uma das toxinas biológicas mais potentes conhecidas, sendo constituídas de duas subunidades, RTA e RTB, unidas por uma ponte de dissulfeto. A RTA (com 267 resíduos) é uma N-glicosidase que inativa ribossomos eucarióticos e a RTB (com 262 resíduos) é uma lectina responsável pela internalização do complexo RTA-RTB no citosol da célula [1]. Autoridades mundiais têm demonstrado preocupação em relação à toxicidade da ricina devido ao seu potencial uso como armas químicas por grupos terroristas. A ausência de medidas contra o envenenamento por ricina tem contribuído ainda mais para essas preocupações [1]. Desse modo, diversas abordagens de química teórica e computacional têm sido empregadas para obter informações acerca dos mecanismos de inibição da ricina, na qual a RTA é o principal alvo de candidatos a inibidores.

Metodologia

Nesse trabalho, realizamos cálculos *single-point* das energias de ligação para seis estruturas do complexo RTA-ligante: RTA-19M (PDB: 4HUP), RTA-RS8 (PDB: 4HUO), RTA-0RB (PDB: 4ESI), RTA-1MX (PDB: 4MX1), RTA-JP2 (PDB: 3PX8) e RTA-JP3 (PDB: 3PX9) e comparamos os resultados com dados experimentais de IC_{50} . Todos os complexos foram relaxados e equilibrados através de simulações de DM [2], sendo que o último frame da trajetória foi utilizado para realização dos cálculos do ΔE_{bind} através do método QM/MM ONIOM [3]. Para todos os cálculos, utilizamos os critérios padrão para cálculos QM/MM ONIOM [3] do programa Gaussian 09. Na parte QM da RTA e dos complexos RTA-ligante, foram utilizados os funcionais B3LYP [4], ω B97X-D [5] (que inclui correções de dispersão DFT-D2) e funções de base 6-31+G(d). Na parte MM foi utilizado o campo de força universal UFF. A parte QM da proteína RTA (189 átomos), incluiu os seguintes resíduos: Glu-177, Arg-180 (importantes para a catálise enzimática), Tyr-80, Val-81, Gly-121 e Tyr-123 (importantes para a ligação e reconhecimento do sítio ativo) [1]. Além desses, incluímos os resíduos Asn-122, Ser-176, Asn-209, Gly-212 e Arg-213 que estão a cerca de 3,0 Å de distância de algum dos seis ligantes, produzindo interações do tipo ligação

de hidrogênio. As energias de ligação para os complexos RTA-ligante foram calculadas de acordo com a seguinte equação:

$$\Delta E_{bind} = \Delta E_{QM/MM}^{RTA-ligante} - (\Delta E_{QM}^{ligante} + \Delta E_{QM/MM}^{RTA})$$

Resultados

Tabela 1: Energias de ligação, ΔE_{bind} (em hartrees) para os seis complexos RTA-ligante obtidos através de cálculos *single-point* QM/MM ONIOM.

Complexo	IC_{50} (μ M)	$\Delta E_{bind}/$ B3LYP (au)	$\Delta E_{bind}/\omega$ B97X -D (au)
19M	15 (1)	-0,136 (1)	-0,230 (1)
RS8	20 (2)	-0,119 (2)	-0,202 (2)
0RB	70 (3)	-0,106 (3)	-0,178 (3)
1MX	209 (4)	-0,062 (6)	-0,130 (4)
JP2	230 (5)	-0,070 (4)	-0,129 (5)
JP3	380 (6)	-0,057 (5)	-0,088 (6)

Ao analisarmos os resultados da Tabela 1, verificamos que os cálculos *single-point* QM/MM ONIOM com o funcional B3LYP foram capazes de identificar os três melhores ligantes (19M, RS8 e 0RB), apresentando uma correlação de 0,929 com os dados de IC_{50} . A única exceção foi o ligante 1MX que apresentou $\Delta E_{(bind)}$ menor que com os ligantes JP2 e JP3. Quando mudamos o funcional B3LYP para o funcional ω B97X-D, que inclui correções de dispersão DFT-D2, verificamos que correlação aumentou de 0,929 para 0,972. Além disso, os resultados obtidos com funcional ω B97X-D classificaram corretamente todos os ligantes de acordo com dados de IC_{50} .

Conclusões

Os cálculos das energias de ligação obtidas através de métodos QM/MM ONIOM apresentaram boas correlações com dados experimentais de IC_{50} , sendo que a performance é aumentada com a utilização de funcionais com correção de dispersão.

Agradecimentos

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Selective vibrational scaling for density functional calculations

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Palavras-Chave: Vibrational Scaling, DFT, Enthalpy of Formation.

Introduction

Chemical bonds involving different atoms usually do not behave like a harmonic oscillator, being necessary to use an anharmonic oscillator to describe the vibrational frequencies of these bonds.

Thermochemical calculations depend on vibrational frequencies and usually the harmonic model is used. To improve the results, a scaling constant is multiplied by the force constants or frequencies to mimic the anharmonic effects.

The objective of this work is to analyze the sensitivity of enthalpies of formation with a selective scaling adjustment dependent of the molecular specie.

Methodology

The selective scaling¹ was applied to 10 different functionals: PBE0, TPSSh, B3LYP, B3LYP-D3, CAM-B3LYP, M05, M06, M11, wB97X, and wB97XD, with 6-31+G(2df,p). A set of 248 reference enthalpies of formation were used to provide the optimum scaling parameters. The reference enthalpies were taken from the G3/05² test set.

Results and Discussion

Table 1 shows the results with no scaling, with scaling from the literature, and corrections 1 and 2. Correction 1 yields the best adjustments of enthalpies of formation for different classes of molecules: saturated hydrocarbons, unsaturated hydrocarbons, substituted hydrocarbons, and molecules that do not belong in any of these groups used the scaling from the literature. Correction 2 is similar to correction 1 except the last class of molecules used the harmonic approximation.

Table 1: Mean absolute error in kcal mol⁻¹ for the 248 molecules of the G3/05² group.

Functional	Scaling of Literature	No Scaling	Correction 1	Correction 2
PBE0	8.47	7.13	4.70	4.66
TPSSh	6.46	5.78	5.23	5.16
B3LYP	5.45	6.23	4.98	4.95
B3LYP-D3	5.81	4.76	3.70	3.63
CAM-B3LYP	5.87	5.14	4.55	4.48
M05	7.06	6.40	4.36	4.31
M06	3.95	3.87	3.81	3.80
M11	5.54	4.82	4.30	4.22
wB97X	4.77	3.82	3.06	2.99
wB97XD	4.44	3.60	3.00	2.94

Table 1 shows that depending on the functional the selective scaling for specific classes of molecules can be significant. PBE0 presented the largest mean absolute error when the scaling from the literature or no scaling are used. However, applying selective scaling reduces the absolute error to approximately 4.7 kcal mol⁻¹. For wB97X and wB97XD, the mean absolute error, which is one of the smallest, is further reduced by 1 kcal mol⁻¹ by the selective scaling.

Table 2 shows the ratio between the scaling factor with respect to experimental frequencies ("anharmonic scaling") and results from correction 2 ("empirical scaling"), or $V = \left[\frac{\text{Empirical Scaling}}{\text{Anharmonic Scaling}} \right] \times 100\%$.

Table 2: Value in percentage of empirical scaling in relation to anharmonic scaling

Functional	Group	Scaling for group
M05	Hydrocarbon	16.36
	Substituted	17.74
	Hydrocarbon	
B3LYP	Hydrocarbon	6.14
	Substituted	8.22
	Hydrocarbon	
wB97XD	Hydrocarbon	4.00
	Substituted	5.52
	Hydrocarbon	

The comparison for these three functionals shows that the empirical scaling from enthalpies of formation is still smaller than the anharmonic adjustment. Table 2 also shows that the functionals are extremely sensitive to the adjustment providing larger or smaller corrections depending on the nature of the functional.

Conclusion

The results show that the use of a single scaling factor for all molecules can provide significant errors for the calculation of enthalpies of formation. The adjustment is also very dependent of the nature of the functional and can reduce drastically the error of calculated thermochemical data.

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Estudo computacional do mecanismo da reação $\text{CH}_4 + \text{CH} \longrightarrow \text{C}_2\text{H}_4 + \text{H}$

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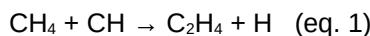
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Palavras-Chave: Mecanismo de reação, estrutura eletrônica, perfil de energia.

Introdução

Dentro do contexto das mudanças climáticas, o aumento da concentração dos gases do efeito estufa (GEE) vem recebendo bastante atenção da comunidade científica. Nesse quesito, o aumento de 3,65% da concentração do gás metano por década caracteriza um impacto de 20% no aquecimento global vigente, justificando a necessidade de encontrar alternativas ao seu uso [1]. A produção de combustíveis e/ou produtos orgânicos de maior valor agregado é uma dessas alternativas com potencial para solucionar tanto a questão ambiental como a geração de energia. Dessa forma, a tecnologia de plasmas químicos oferece um meio plausível para promover o aumento da cadeia carbônica e, assim, obter produtos de interesse menos danosos e de grande utilidade econômica [2]. A eq. 1 representa uma das reações que podem ser exploradas, cujo produto satisfaz os fatores mencionados anteriormente. Portanto, a aplicação de metodologias da Química Computacional podem contribuir diretamente para o entendimento da dinâmica e dos processos cinéticos envolvidos na reação em questão.



Metodologia

Foram realizados as otimizações das geometrias de 10 pontos estacionários no nível CCSD(T)/cc-pVTZ por meio do programa MOLPRO (2020.2). Com isso, pretende-se aplicar melhoramentos na energia eletrônica dessas espécies ao incluir nas respectivas energias o limite de bases completas (CBS), efeitos relativísticos escalares, correlação caroço-valência e excitações de ordem superiores.

Resultados

O perfil de energia obtido para a reação dada pela eq.1 está representado pela Figura 1. Como se pode observar, esse mecanismo caracteriza um efeito inverso de Arrhenius, dada pela barreira potencial negativa em TS1. Esse efeito também foi observado experimentalmente [3].

As entalpias de reação para o caminho reacional majoritário (c) [3] foram calculadas em vários níveis de estrutura eletrônica (Tabela 1). Esses resultados validam o procedimento e permitem a aplicação das correções na energia eletrônica como próximo passo.

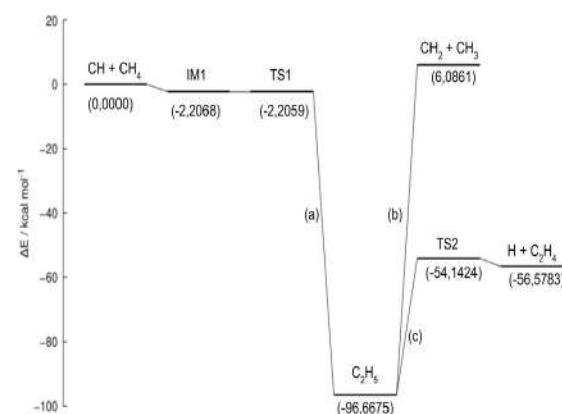


Figura 1: Perfil de energia do mecanismo da reação entre CH e CH_4 no nível CCSD(T)/cc-pVTZ

Tabela 1: Entalpia de reação para o caminho (c) a 298,15 K

Nível de teoria	$\Delta_r H^\circ / \text{kcal mol}^{-1}$	Erro %
MP2/cc-pVTZ	-64,95	8,16%
MP2/aug-cc-pVTZ	-65,08	8,37%
MP2/aug-cc-pVQZ	-66,14	10,13%
CCSD(T)/cc-pVTZ	-55,57	7,46%
CCSD(T)/aug-cc-pVTZ	-55,50	7,59%
CCSD(T)-F12b/VTZ-F12	-57,49	4,28%
Experimental	-60,06	

Conclusões

Com base nas comparações entre as entalpias de reação, o método CCSD(T)/cc-pVTZ é capaz de descrever as propriedades termoquímicas com precisão considerável, além de descrever a barreira negativa centrada no TS1 responsável pelo efeito mencionado.

Agradecimentos

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QM/MM Transition Path Sampling Study of Serine Hydrolase Mechanism

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Palavras-Chave: Feruloyl Esterase, Likelihood Maximization, Reaction Coordinate

Serine hydrolases cleave peptide and ester bonds and are ubiquitous in nature, with applications in biotechnology, in materials, and as drug targets. The serine hydrolase two-step mechanism employs a serine–histidine–aspartate/glutamate catalytic triad, where the histidine residue acts as a base to activate poor nucleophiles (a serine residue or a water molecule) and as an acid to allow the dissociation of poor leaving groups. This mechanism has been the subject of debate regarding how histidine shuttles the proton from the nucleophile to the leaving group.

To elucidate the two-step reaction mechanism of serine hydrolases, we employ quantum mechanics/molecular mechanics-based transition path sampling to obtain the reaction coordinate using the *Aspergillus niger* feruloyl esterase A (AnFaeA) as a model enzyme. The method allows the study of rare events without the a priori definition of reaction coordinates or use of biasing potentials. The optimal reaction coordinates, obtained a posteriori from an ensemble of 25,000 trajectories crossing the transition interface with a supervised learning-like approach, include terms involving nucleophilic attack on the carbonyl carbon and proton transfer to, and dissociation of, the leaving group.

During the reaction, the histidine residue undergoes a reorientation on the time scale of hundreds of femtoseconds that supports the “moving histidine” mechanism (Figure 1), thus calling into question the “ring flip” mechanism. We find a concerted mechanism, where the transition state coincides with the tetrahedral intermediate with the histidine residue pointed between the nucleophile and the leaving group. Moreover, motions of the catalytic aspartate toward the histidine occur concertedly with proton abstraction by the catalytic histidine and help stabilize the transition state, thus partially explaining how serine hydrolases enable poor nucleophiles to attack the substrate carbonyl carbon. Rate calculations, based on the reaction flux formalism, indicate that the second step (deacylation) is rate-determining, with a calculated rate constant of 66 s^{-1} .

Overall, these results reveal the pivotal role of active-site dynamics in the catalytic mechanism of AnFaeA, which is likely similar in other serine hydrolases.

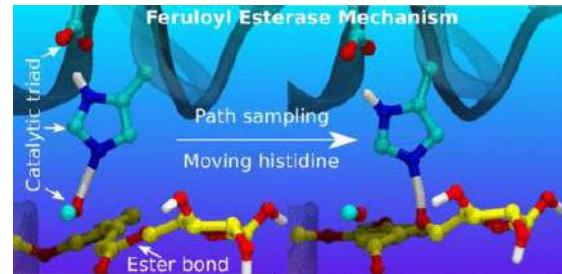


Figure 1: Illustration of the moving histidine mechanism based on unbiased reactive trajectories generated with transition path sampling.

Estudo teórico da adsorção de metais alcalinos no grafeno

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Palavras-Chave: Grafeno, DFT, adsorção de metais.

Introdução

O grafeno é uma forma alotrópica do carbono, que tem apenas duas dimensões, formado apenas por uma folha de carbono com hibridização do tipo sp^2 . Por causa da sua conjugação eletrônica e geometria, o grafeno tem diversas propriedades, tais como: alto módulo de elasticidade e mobilidade de carga, alta área de superfície.

Atualmente a intercalação de átomos de lítio no meio de folhas de grafeno, que juntas formam o grafite, é um dos materiais usados como ânodos em baterias de íon-lítio. Contudo, a escassez de lítio na superfície terrestre e seu alto custo traz a tona a necessidade de se pesquisar materiais com propriedades similares e com menor custo, dessa maneira surgem pesquisas da adsorção de outros metais alcalinos, como o sódio¹ e potássio², e metais alcalinos terrosos, no grafeno ou a intercalação desses mesmo metais em duas ou mais folhas de grafeno. Portanto, o objetivo desse trabalho é estudar a adsorção de metais alcalinos em uma e duas folhas de grafeno.

Metodologia

Foi utilizado um modelo periódico aplicado no programa VASP com a Teoria do Funcional Densidade (DFT) com os seguintes funcionais: PBE, *Perdew-Burke-Ernzenhof*, com a aproximação GGA, *Generalized Gradient Approximation*, e com outras correções para descrever melhor as interações dispersivas presentes nos sistemas estudados: PBE com a correção D2 e PBE com a correção D3-BJ.

As informações eletrônicas dos sistemas estudados foram obtidas através da densidade dos estados (DOS) e da função de localização dos elétrons (ELF).

Resultados

O trabalho da adsorção de metais em uma folha de grafeno foi realizado com uma célula unitária com 72 átomos de carbono, sendo que esse tamanho foi escolhido após a comparação entre o custo computacional e o resultado energético de células de vários tamanhos.

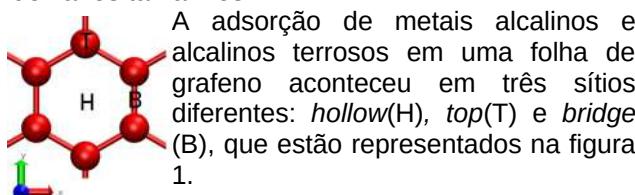


Figura 1. Representação dos sítios de adsorção estudados.

A energia de adsorção, presentes na figura 2, para esses sistemas foi definida da seguinte forma:

$$E_{ads} = E_{Folha+Metal} - E_{Metal} - E_{umaFolha}$$

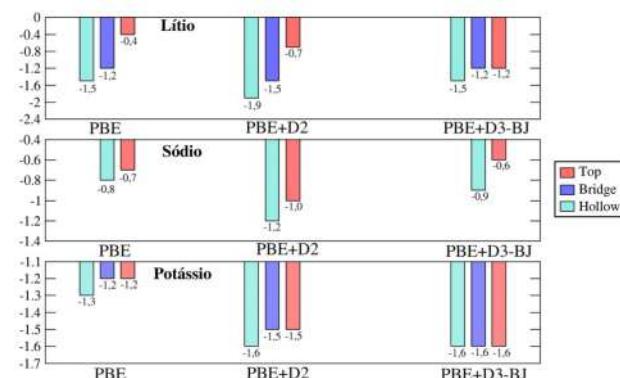


Figura 2. Energia de adsorção entre o grafeno e os metais alcalinos nos sítios de adsorção mencionados anteriormente.

Os resultados energéticos apresentados mostram que a interação é maior entre o lítio e uma folha de grafeno, na posição *hollow* com o funcional PBE+D2, do que com outros metais estudados, além disso a interação entre uma folha de grafeno e o sódio é bem mais fraca, sendo inclusive instável no sítio *bridge*. Ademais, a interação entre o potássio e uma folha de grafeno se mostrou mais estável que a do lítio nas posições *top* e *bridge*, com alguns dos funcionais estudados.

Conclusões

Conclui-se através dos resultados apresentados que o melhor sítio de absorção para os três metais estudados é o *hollow*, sendo que maior interação ocorre entre uma folha de grafeno e o lítio, na posição *hollow* com o funcional PBE+D2, o que pode ser um indício de um caráter covalente na ligação entre o metal e o substrato.

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Unveiling the Molecular Structure of Antimalarial Drugs Chloroquine and Hydroxychloroquine in Solution through Analysis of ^1H NMR Chemical Shifts

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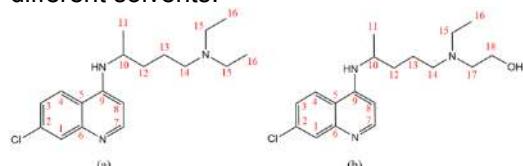
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Palavras-Chave: DFT, NMR, MD

Introduction

Chloroquine (CQ) and hydroxychloroquine (HCQ) whose structures are shown in Scheme 1 have been standard antimalarial drugs since the early 1950s^{1,2}, and very recently, the possibility of their use for the treatment of COVID-19 patients has been considered. Research groups have dedicated efforts to understand the action of the virus, to seek drugs that, somehow, could reduce or eliminate the biological activity of the virus in the human body, developing studies in the most diverse areas of knowledge^{3,4}. In the present study, DFT calculations and Molecular Dynamics simulations were carried out to get thermodynamic and structural information and describe the Molecular Structure of CQ and HCQ in different solvents.



Scheme 1. Structural formulas of CQ (a) and HCQ (b) and the numbering scheme adopted

Methodology

This first optimized structure was named M1 (conformation 1) and used as a starting point for an extensive conformational search varying eight dihedral angles (indicated in Figure 1) in an attempt to address all possible conformations plausible to exist in solution. Thirty distinct fully optimized structures were obtained using this procedure, which we expect to represent faithfully the relevant spatial arrangement of CQ and HCQ in solution. All structures were optimized at ω B97x-D/6-31G(d,p) - PCM level of theory, and did not present imaginary frequencies were computed for the solvents water, chloroform and DMSO. Molecular dynamics (MD) simulation was carried out aiming to find further plausible structures that might have been missed in our systematic conformational search. The structures of CQ and HCQ were prepared for MD simulation using the antechamber module of the Amber program.

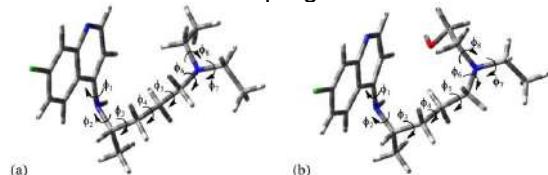


Figure 1. ω B97x-D/6-31G(d,p)-PCM -water optimized structure of conformation M1 of CQ (a) and HCQ (b) molecules and definition of torsion angles ($\phi_1, \phi_2, \phi_3, \phi_4, \phi_5, \phi_6, \phi_7, \phi_8$).

Results

The ω B97x-D/6-31G(d,p)-PCM-water optimized torsion angle values defined in Figure 1 for 32 minimum-energy structures located on the PES for CQ and HCQ (structures M31 and M32 are originated from MD simulation in water). Based on the analysis of ^1H NMR theoretical and experimental profiles, the observed chloroquine structure in

D_2O is definitively M12 and not the thermodynamic preferred H-bonded structure M24.

The Figure 2 shows a schematic representation of fragment from photochemical degradation of chloroquine. The gradual improvement of the B3LYP N–H chemical shift value as the number of explicit solvent molecules increase is promptly seen, providing strong support to the efficaciousness of inclusion of explicit solvent molecules in DFT calculations of ^1H NMR chemical shifts for N–H protons. In the case of this small fragment addition of three solvent molecules in the geometry optimization procedure, it was enough to correctly reproduce the N–H NMR signal.

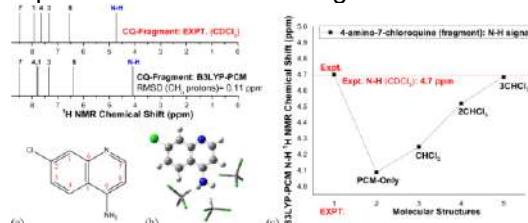


Figure 2. (a) Schematic representation and (b) ω B97x-D/6-31G(d,p)-PCM -chloroform fully optimized structures of fragment I of chloroquine including three explicit CHCl_3 solvent molecules. (c) Experimental N–H chemical shift data (horizontal red line) and B3LYP/6 31G(d,p)-PCM-chloroform ^1H NMR values calculated

Conclusions

Based on the spectroscopic criterion, there are two main structures predicted as good candidates as the observed molecular structure of chloroquine and hydroxychloroquine, M12 in D_2O and M8 in CDCl_3 and DMSO-d_6 , showing the solvent influence on the molecular structure present in solution. In addition, MD simulations in water were performed in an attempt to locate other plausible structures generating two new averaged molecular structures in 70 and 30% of the frames, named MD1 and MD2, respectively. The B3LYP-PCM ^1H NMR chemical shifts for these optimized structures (ω B97x-D/6-31G(d,p)-PCM-water level) did not lead to an improvement in agreement with experimental NMR data in solution, and so they could be discarded, indicating that our quantum chemical structural sampling was adequate.

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A geometric interpretation for coupled-cluster theory being more accurate than corresponding configuration interaction

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Keywords: Coupled-cluster, optimization.

Introduction

Coupled-cluster (CC) theory is one of the most successful theories for electronic structure,¹ because it can very accurately recover large portion of correlation energy, for single-reference systems, at a reasonable computational cost. It is based on the exponential *ansatz* for the wave function:

$$|\Psi_{\text{CC}}\rangle = e^T |\Phi_{\text{HF}}\rangle, \quad (1)$$

that is defined through the *amplitudes*, t_p , that are the parameters that make the cluster operator,

$$T = \sum t_p T_p. \quad (2)$$

The summation runs over a fixed set of excitation operators, T_p , usually single and doubles leading to the CCSD method.

Although coupled-cluster theory is very well established, with a well known procedure to obtain the amplitudes, few attention is given to the set of wave functions that can be cast as in Equation (1): If we consider all wave functions that can be expressed in this way, for all possible amplitudes, we obtain a submanifold of the wave functions space, the *coupled-cluster manifold*. On the other hand, the set of all wave functions that can be expressed as in the *ansatz* of the configuration interaction (CI) method:

$$|\Psi_{\text{CI}}\rangle = (1 + T) |\Phi_{\text{HF}}\rangle, \quad (3)$$

defines the manifold associated to the configuration interaction method. Note that the number of parameters that define both the coupled-cluster and the configuration interaction manifolds is the same, and these manifolds have the same dimension.

The coupled-cluster method is considered to be more accurate than the configuration interaction method, in particular because it is size-extensive.² The objective of this work is to investigate if this higher accuracy is related to the distance between the full-configuration interaction (FCI) wave function and the manifolds associated to these two methods.

Methodology

We have developed an algorithm to find the point of the coupled-cluster-manifold closest to the FCI wave function (in the intermediate normalization) by the Newton method. The coupled-cluster amplitudes are converted to coefficients of Slater determinants using the cluster decomposition of wave functions, described in reference [3]. Main equations have been derived using standard techniques of electronic structure theory² and implemented in our local code using Python/Cython.

Results

We have calculated, for four (H_4) and six (Li_2) electron systems, the distances (D) from the FCI wave function and the CCSD and CISD manifolds. The results for Li_2 are shown below:

- The FCI wave function is always closer to the CCSD manifold than to the CISD manifold;
- More accurate energies occur when the distance to the FCI wave function is low;
- Larger distances observed in the dissociation limit are due to large distances to the reference, restricted Hartree-Fock, wave function.

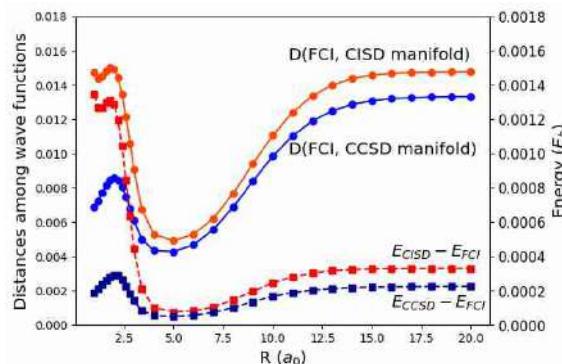


Figure: The energy error of the CCSD and the CISD methods, and the distances from the FCI wave function to the corresponding manifolds, for Li_2 calculated with the 6-31G basis set.

Conclusions

For the selected molecular systems that we investigated, we observed that the higher accuracy of the coupled-cluster method, as compared to the configuration interaction method, is associated to the exact wave function being closer to the coupled-cluster manifold than to the configuration interaction manifold.

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Characterization and metal-ligand interaction study between xanthate ligand and nickel (II)

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Palavras-Chave: Xanthate, Nickel, DFT.

The xanthate ligand, O-alkyldithiocarbonates, a useful flotation agent, has an easy and inexpensive synthesis [1]. Recently, the literature reported many different applications using xanthate complexes with several metals cation [2]. The nickel metal has its many application in the battery, welding and catalysis industry, and is known as a hazardous heavy-metal for the human body [3,4]. The xanthate ligand may be a practical solution for the removal of nickel(II) from industrial wastewater. Therefore, the objective of this study is to characterize the xanthate complex with Ni(II) using 3 alkyl variations of the ligand (ethyl, n-propyl and n-butyl).

The theoretical calculation, realized for the xanthate complex with Ni²⁺, using different alkyl xanthate derivate (ethyl, n-propyl, n-butyl), was performed with the DFT method M06L, using the basis set 6-311+G(d,p) for the light atoms (C, O, S, H) and LANL2TZ-ECP for the Ni atom. The electronic structure, its normal modes, the UV-Vis spectroscopy, the energy decomposition analysis (EDA) and natural bond orbital (NBO) calculations were used to investigate the components and parameters associated with the increase of the hydrocarbon chain of the ligand and its effects on the overall interaction.

The xanthate complex with nickel metal cation follows a symmetrical C_{2h} structure with no correlation between the bond length and the number of carbon atoms in the molecule. Although, the Mulliken charges found on the metal and on the ligand bridging spot (S-C=S) shows a direct correlation with the ligand size, by increasing the negative charge on the metal cation and increasing the positive charge on the SCS fragment. This behavior can be further explored using bond analysis as EDA and NBO calculations.

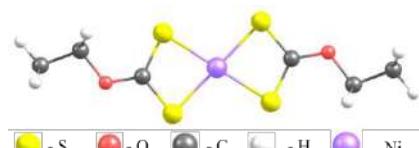


Figure 1: Molecular C_{2h} structure for ethylxanthate complex with Ni²⁺.

The EDA analysis performed on the nickel complex with the xanthate complex presented an electrostatic interaction between the ligand and the

metal cation. The analyses were calculated using two different separations: metal + ligand as one fragment, isolating the other ligand; and considering the metal as one fragment and the two ligands as the second fragment. This analysis shows a decreasing covalent character as the number of carbon atom increases.

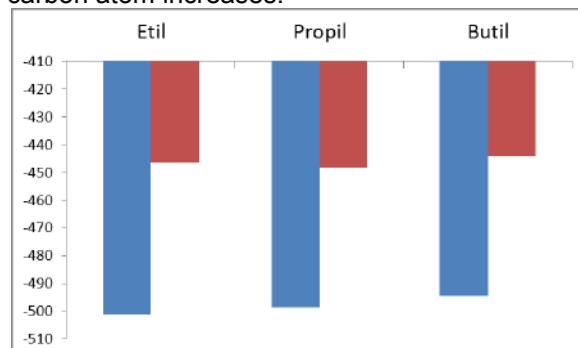


Figure 2: EDA analysis with the component electrostatic (blue) and covalent (red) for the xanthate complex with Ni(II).

This fact can be supported by the NBO analysis and the donor-acceptor energy (E_{DA}) that presents the same tendency. There was no significant variation for the orbital hybridization for all complexes and the ligand orbitals were characterized as p lone pair for the sulfur atom interaction with a s and d lone pair of Ni(II) atom. Besides this interaction, the S=C bond presented significant E_{DA}, with the interaction between the same nickel orbital and the π SC bond, with a higher participation for the sulfur atom.

The study will also clarify the influence of the alkyl fragment on the spectroscopy analysis and how the symmetry and arrangement of the complex influence the electrostatic behavior found.

Acknowledgements: The authors acknowledge FAPERJ, CNPQ, PROPPU-UFF, LMQC.

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Efeitos do 2,2,2-Trifluoroetanol no equilíbrio conformacional do peptídeo (AAQAA)₃

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Palavras-Chave: 2,2,2-Trifluoroetanol, alfa-hélice, Dinâmica Molecular com amostragem ampliada.

Introdução

2,2,2-Trifluoroetanol (TFE) possui efeitos estabilizadores em peptídeos e proteínas. Um dos principais efeitos do TFE nesses sistemas é a capacidade de induzir a formação de hélices, especialmente se a sequência de aminoácidos apresentar uma tendência para essa estrutura secundária¹. Embora a habilidade do co-solvente na estabilização e indução de hélices em peptídeos e proteínas tenha sido relatada em trabalhos experimentais e teóricos, o mecanismo exato de ação do TFE ainda não foi totalmente elucidado. Este trabalho tem como objetivo caracterizar as estruturas de solvatação de um peptídeo em água e em solução de TFE a partir de simulações de Dinâmica Molecular (DM) com troca de réplicas. Os efeitos do TFE no equilíbrio conformacional de peptídeos serão abordados utilizando as funções de distribuição de mínima distância² (MDDFs - do inglês, *minimum-distance distribution functions*) e a teoria de Kirkwood-Buff³. Com isso, espera-se identificar os possíveis mecanismos de ação do TFE.

Metodologia

O peptídeo (AAQAA)₃ foi estudado em água e em solução de TFE (60% (v/v)) por meio de simulações de Dinâmica Molecular (DM) com troca de réplicas (método REST²⁴, em que todas as réplicas são simuladas na mesma temperatura, mas as funções de energia são aproximadas). Os sistemas iniciais foram construídos com Packmol⁵ e as simulações foram realizadas com os softwares GROMACS⁶ e Plumed⁷. O conteúdo de alfa-hélices do peptídeo foi calculado com o software DSSP. Espectros teóricos de dicroísmo circular (DC) foram determinados com o software SESCA. Finalmente, os efeitos do solvente no equilíbrio conformacional do peptídeo foram estudados com o pacote [ComplexMixtures.jl](#). A estrutura do solvente foi caracterizada pelas MDDFs². Com as MDDFs, e também a concentração dos solventes no *bulk* da solução foi possível determinar as integrais de Kirkwood-Buff (IKB) e os Parâmetros de Solvatação Preferencial.

Resultados

As distribuições do raio de giração do peptídeo evidenciaram a presença de estruturas mais compactas na solução contendo TFE. Além disso, o conteúdo de alfa-hélices atribuído pelo DSSP, e os

espectros teóricos de dicroísmo circular, indicam favorecimento das hélices na solução de TFE em relação à água pura, como esperado. Por meio das MDDFs foi possível obter uma visão molecular da forma com que as moléculas de solvente se distribuem na solução. Resumidamente, os resultados mostraram que o hidrogênio ácido do TFE interage diretamente por meio de ligações de hidrogênio (LHs) com o oxigênio da cadeia principal do peptídeo, mas nenhuma LH é observada com o nitrogênio amídico. Por outro lado, o número de LHs entre as moléculas de água e o peptídeo é cerca de três vezes menor na presença de TFE. Vale destacar que além das LHs com a cadeia principal do peptídeo, interações não específicas do TFE com o peptídeo também ocorreram. De forma complementar, o parâmetro de solvatação preferencial sugere que o peptídeo é preferencialmente solvatado pelo TFE.

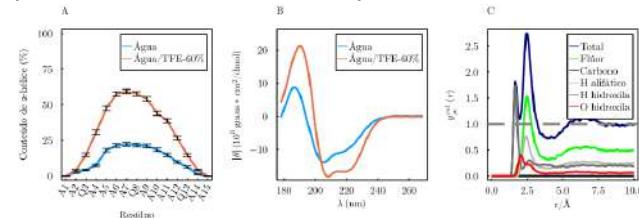


Figura 1. A) Conteúdo de alfa-hélices; B) Espectro de dicroísmo circular e C) MDDF do TFE.

Conclusões

Os resultados suportam a proposta de que as LHs intermoleculares entre o hidrogênio ácido do TFE e o oxigênio da carbonila estejam preservando as LHs intramoleculares entre o nitrogênio amídico e o oxigênio da carbonila, contribuindo para estabilização das hélices. O TFE também se acumula de forma inespecífica em torno do peptídeo, enquanto que a estrutura da água é perturbada nas vizinhanças do peptídeo.

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Thermodynamic and Structural Description of Relative Solubility of Rutin by DFT Calculations and Molecular Dynamics Simulations

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Keywords: DFT, MD, Solubility.

Introduction

Rutin (a known antioxidant and anticancer), despite having two units of saccharides in its structure and many OH groups, presents a very low solubility in water¹. In the present study, Density Functional Theory (DFT) calculations and Molecular Dynamics (MD) simulations were carried out to get thermodynamic and structural information and describe the relative solubility of this polyphenol in different solvents.

Methodology

Our starting point geometry was optimized at the ω B97x-D/6-31G(d,p)-PCM level of calculation (having no imaginary frequency) in our previous work². The ΔG_{solv} (in PCM model) were computed for the solvents water, ethanol, 1-propanol, 2-propanol, acetone and heptane. MD simulations were performed using the TrPPE force field for organic solvents, GAFF for model rutin and the TIP4P model for water. The steps were the box construction, two NpT equilibrations and a NpT production simulation. The ΔG_{solv} was calculated in a perturbative approach in 14 states, so that the interactions of vdW and electrostatics were controlled by λ_m . The results were analyzed by the PyMBAR software, and the relative solubility was compared using the free energy of transference

$$(\text{TFE} = \ln \left(\frac{c_i}{c_{\text{water}}} \right)) = \beta \mu_{\text{water}}^{\text{res},\infty} - \beta \mu_i^{\text{res},\infty}$$

Results

The solvation free energies were calculated using MBAR and DFT methods, whose results are shown in Figure 1. The MBAR data (Fig 1a) showed a good agreement with the experimental solubilities, especially for water, methanol, and ethanol, with some fluctuations for the other alcohols. The DFT results (with and without the DIS, REP and CAV keywords) presented very different patterns, but the results with the active keywords were better (Fig 1b).

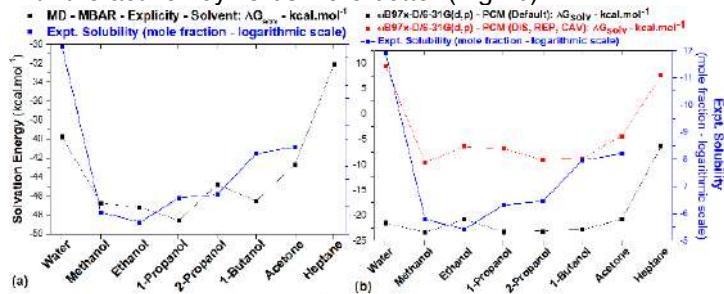


Figure 1. Comparison between ΔG_{solv} and exp. solubilities.

The contributions of each type of intermolecular interaction between solute and solvent provide important information about the solvation process. Figure 2 shows the electrostatic and dispersive contributions for ΔG_{solv} . It is possible to conclude that the solvation of rutin in solvents with very high or very low polarity is unfavorable (pink rectangles) and becomes more favorable for solvents capable of performing both types of interaction (purple rectangles).

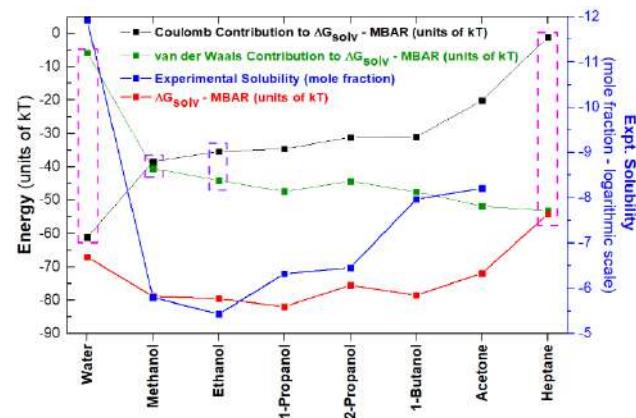


Figure 2. Decomposition of the MBAR ΔG_{solv} in van der Waals and Coulombic contributions (units of kT).

Corroborating these results, the radial and spatial distribution functions were generated to map intermolecular interactions (Figure 3). It is possible to notice that the peak intensities for RDFs in rutin-ethanol system are higher than in rutin-water system, which is consistent with experimental observation. In addition, SDFs reveal that ethanol can interact with the OH groups of rutin and with CH_n hydrophobic groups, which favors the solvation and agrees with Figure 2.

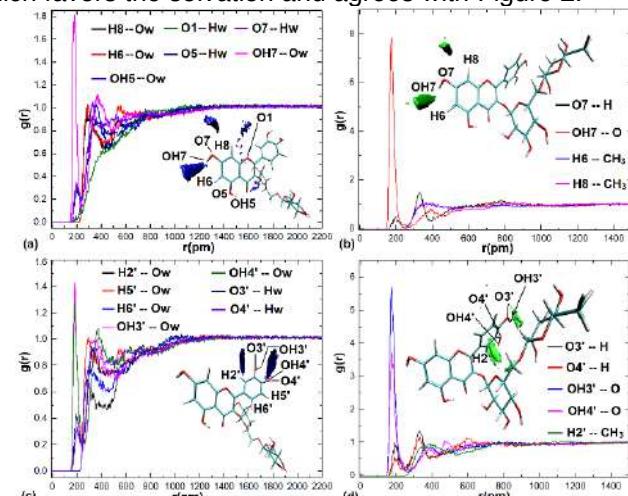


Figure 3. RDF and SDF for rutin-ethanol and rutin-water systems.

Conclusions

Based on the thermodynamic and structural data presented, it is possible to conclude that rutin solvation is favored in solvents capable of performing electrostatic and dispersive interactions (such as lower chain alcohols).

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A theoretical study of poly(*p*-phenylenes) and their cyclodextrin-based insulated molecular wires

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Keywords: Conjugated polymers, HOMO-LUMO gap, Push-pull groups.

Introduction

The π -electron conjugated polymers (CPs) have been recognized as alternative and promising candidates in the electronic device fabrication.¹ However, a fundamental requirement for adequate development, processing, and application of CPs as a molecular electronic device is the solubility.² In this sense, an efficient strategy to improve the solubility of CPs is the formation of inclusion complexes with cyclodextrins (CDs), also known as CD-based insulated molecular wires (MWs) (Fig.1).³

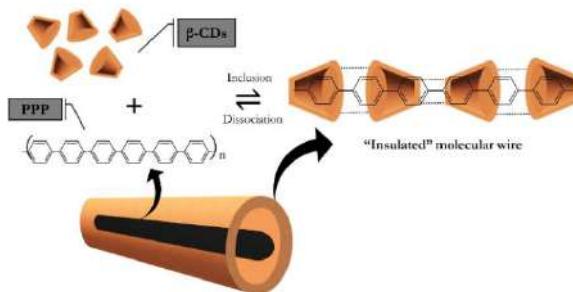


Figure 1: Schematic representation of the CD-based insulated molecular wires formation process.

In this work, we have performed a theoretical investigation via Semiempirical and Density Functional Theory (DFT) calculations in order to evaluate structural and electronic properties related to pristine poly(*p*-phenylene) oligomers (PPPs) and *push-pull* derivatives and their respective β -cyclodextrin (β -CD) based insulated molecular wires (MWs).

Results and discussions

In the first stage of this research, we have observed that the PPP oligomer substituted by the NH_2/NO_2 *push-pull* group (Fig.2) presented the lowest HOMO-LUMO gap (E_g) among all studied. As can be seen in Table 1, after the encapsulation process of two selected structures (pristine $(\text{PPP})_4$ and $[\text{NH}_2-(\text{PPP})_4-\text{NO}_2]$ derivative) into β -CD dimeric tube, both MWs exhibited nearly the same E_g in comparison to those respective isolated oligomers. This result is quite relevant since both pristine and substituted oligomers covered by β -CDs were able to maintain their original conductive properties. Also, it is possible to observe in Table 1 that the μ value for MW is much higher than that obtained for the isolated oligomer, which indicates a substantial increase in the PPP

polarity when it is on the insulated form. This result shows the increased PPP polarity in the form of an inclusion complex, which indicates the increased solubility of this polymer in traditional organic solvents, such as polar ones.

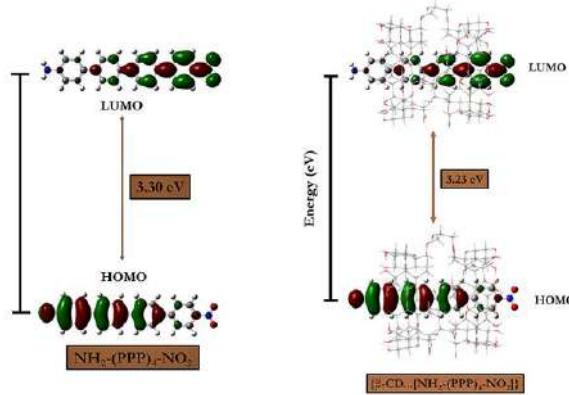


Figure 2: HOMO-LUMO gaps diagrams and contour plots for $\text{NH}_2-(\text{PPP})_4-\text{NO}_2$ oligomer and $\{\beta\text{-CD}...[\text{NH}_2-(\text{PPP})_4-\text{NO}_2]\}$ molecular wire.

Table 1. HOMO-LUMO gaps (E_g) and dipole moments (μ) for the isolated $(\text{PPP})_4$ and $[\text{NH}_2-(\text{PPP})_4-\text{NO}_2]$ and their respective molecular wires calculated at the PBE1PBE/6-31G(d,p)/PM3 level

	Compounds	E_g (eV)	μ (D)
PPP Isolated	$(\text{PPP})_4$ pristine	4.20	2.4
	$[\text{NH}_2-(\text{PPP})_4-\text{NO}_2]$	3.30	5.3
	$[\beta\text{-CD}...(\text{PPP})_4]$	4.15	5.8
	$\{\beta\text{-CD}...[\text{NH}_2-(\text{PPP})_4-\text{NO}_2]\}$	3.23	10.5

Conclusions

As a main result, we concluded that the conductive properties of PPPs were maintained after the isolation process in β -CD dimeric tube. We also show that PPP oligomers are more polar in nature due to molecular inclusion. Finally, we strongly believe that the use of PPPs in the form of insulated molecular wires is a promising and feasible approach to explore in future experimental investigations. It is noteworthy that this work was recently published [Paulino, P. H. S. et al.; *Comput. Theor. Chem.* **2021**, 1197, 113157].

Acknowledgements

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Modelagem e análise comparativa entre as fosfomanoses isomerases humanas e de *Xanthomonas* sp, para o desenvolvimento de inibidores contra o cancro cítrico.

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Palayras-Chaye: *Cancro cítrico, fosfomanose isomerase, drug design*

INTRODUÇÃO

A fosfomanose isomerase (PMI) é uma enzima que catalisa a interconversão da frutose-6-fosfato (F6P) e da manose-6-fosfato (M6P) além de permitir a síntese do difosfato de guanosina manose (GDP-manoose) em organismos eucarióticos, como o ser humano¹. Essa enzima é considerada como potencial alvo terapêutico por causa da participação na sobrevivência e patogenicidade de diversos microrganismos como, por exemplo, a bactéria *Xanthomonas citri* subsp. *citri* (XAC)². A XAC é causadora da doença cancro cítrico, uma das doenças de citros mais importantes e que provoca um grande impacto na economia brasileira³. O intuito do trabalho é propor um composto capaz de inhibir seletivamente a PMI de XAC encontrada na superfície bacteriana em comparação com a homóloga humana.

METODOLOGIA

O estudo consistiu na construção de modelos da proteína fosfomanose isomerase de *Xanthomonas citri* subsp. *citri* e *Homo sapiens*, por de modelagem por homologia estrutural, já que tais estruturas ainda não foram depositadas no banco de dados de estruturas de proteínas, o Protein Data Bank (PDB). Os estudos de homologia estrutural são baseados em três passos: (1) alinhamento das sequências proteicas, (2) a construção do modelo e (3) a validação do modelo, aqui realizados para posterior uso em triagem virtual em bases de dados.

RESULTADOS

Homo sapiens	-----MAAPFRVPLSCAVQOYK	GKMBNSSEVARLLASSDPLAQIAEDKFTAYL	49
Xanthomonas	MSDVLPII-----GGSGIRLPLRSQEYPKQ-----	FLELPGDKRNLQST	42
	*****	*	
Homo sapiens	KGTHPRCDA-KILDNNRISQKTLQSNI-AENQDSLGK-----		86
Xanthomonas	WLRAAFPVAGHAPIVFVNEE-----HRPMLAQLQLQKPSVAPSAILLEPKGRNTAFALVAAL		95
	*****	*****	
Homo sapiens	KDTFNGNLPFLFKVLSVET-----P-----LS-----I-----A-----	--PNKELAKELMHLNQAPO--HYF-	13
Xanthomonas	EATRGGADPLLVLVFL-----V-----V-----I-----Q-----H-----A-----	KEATRGGADPLLVLVFL-----V-----V-----I-----Q-----H-----A-----	15
	*****	*****	
Homo sapiens	-----DANH-----F-----E-----N-----I-----A-----L-----T-----I-----P-----	--FQSLGCLFRPEEIVTFKLKVWPFQFQFLI	17
Xanthomonas	ASAGAGASAVERFVKPULATIAQSYLASGKYYNNSGMFLRFA-----SRYLEELRKRFPAI		21
	*****	*****	
Homo sapiens	GDEATHLHQIM-----SHDSQAVASSL-QSCFSHLMKSEKKVVVEQILNLVVKRISQQA		22
Xanthomonas	ADACOKENNSWKRDRDFTRLKEDMFAS-----P-----S-----D-----I-----Y-----A-----M-----T-----A-----V-----P-----L-----		26
	*****	*****	
Homo sapiens	AAGNNMEDIFGELLIQLHQVYGP-----DIGGCFAIYFLN-----LILTKEGEAMPLEANV		27
Xanthomonas	DAGNNHDDGSWSLILV3NODAOGNANHGVIOIDCONTYAGSRSLTM-VGLEDVVVET		32
	*****	*****	
Homo sapiens	P-----A-----L-----K-----G-----D-----C-----V-----I-----A-----C-----S-----A-----T-----V-----E-----A-----G-----L-----P-----I-----C-----E-----M-----	--LYTPSSSKD	32
Xanthomonas	PDAYLVGH-----RDR105VKNVN3C01KAGRSEATWHKRYVFRSGWDQ-----		36
	*****	*****	

Figura 1. Alinhamento entre as sequências da fosfomanose isomerase humana e de *Xanthomonas*. Elas compartilham 23%

de identidade sequencial total, mas 20% de identidade e similaridade na região do sítio ativo (sobreposição dos modelos).

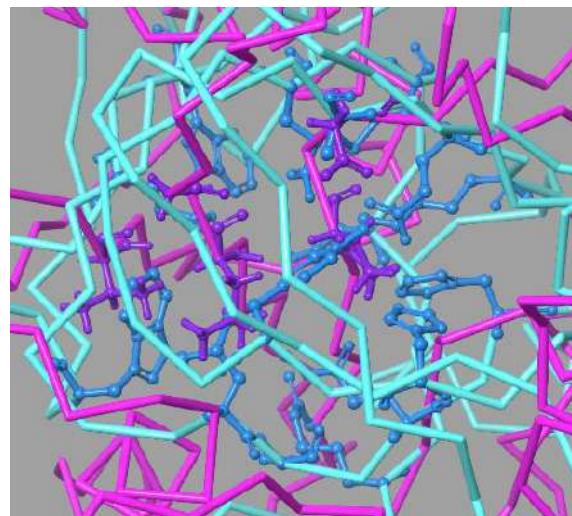


Figura 2. Sobreposição da fosfomanose isomerase humana (ciano) e de *Xanthomonas* sp (rosa), mostrando os aminoácidos que compõem os sítios ativos, respectivamente.

CONCLUSÃO

Os modelos foram bem avaliados com respeito à estereoquímica, contatos atômicos e ambientes químicos e são de extrema importância para o desenvolvimento de inibidores pois permite a visualização das posições dos aminoácidos e suas respectivas interações.

Devido à baixa identidade apresentada entre as fosfomanoses isomerase de XAC e a humana e também às diferenças presentes na região do sítio ativo, torna-se atrativo o desenvolvimento de inibidores seletivos para a PMI de XAC.

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Caracterização teórica de novas moléculas de β -dicetonatos de Difluoroboron Flavanonas.

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Palavras-Chave: Absorção, Orbitais moleculares, TDDFT.

Introdução

A síntese de novas moléculas orgânicas com propriedades específicas vem se tornando cada vez mais importante no desenvolvimento de novos materiais para nanodispositivos como células solares. Através de métodos de primeiros princípios podemos caracterizar compostos como Difluoroboron β -dicetonatos (BF_2dbm)^[1] que exibem fortes características fotofísicas como luminescência e fluorescência em solução e altos coeficientes molarres^[2]. Neste trabalho fizemos a caracterização teórica dessas moléculas para determinar propriedades do estado fundamental e excitado utilizando Teoria do Funcional da Densidade (DFT)^{[2]-[3]} e sua extensão dependente do tempo (TD-DFT)^[4], respectivamente.

Metodologia

Os cálculos foram realizados utilizando os formalismos DFT e TD-DFT implementados no programa ORCA^[5]. O funcional híbrido B3LYP^[6] foi escolhido para representar o potencial de troca correlação. Cálculos foram realizados considerando fase gasosa e também utilizando o modelo (CPCM)^[7] para caracterização do sistema sob efeitos de diferentes solventes. TDDFT foi usado para descrever os níveis eletrônicos envolvidos nas excitações e para os cálculos de absorção óptica.

Resultados

A molécula 4a apresentou na fase gasosa uma absorção máxima em 379.4 nm e um segundo pico em 328 nm, concordando com a literatura^[8]. Percebemos um red shift de 41 nm para diferentes solventes com diferentes polarizabilidades, sem mudança considerável na densidade dos orbitais e contribuição na transição. Para as moléculas 4b, 4c e 4d, os picos máximos na fase gasosa são 377.2

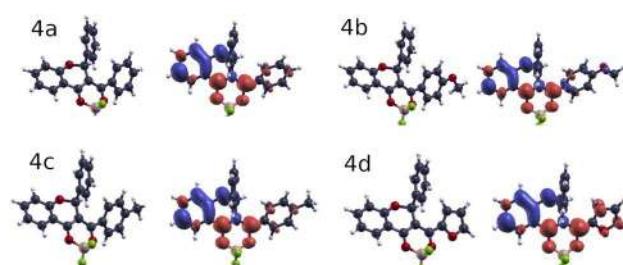


Figura 1: Orbitais moleculares e TDDFT para primeiro estado excitado para cálculos TDDFT completos para as moléculas 4a, 4b, 4c e 4d.

nm, 374.7 nm e 386 nm, com red shifts de 27.5 nm, 39.7 nm, 42.2 nm, respectivamente de acordo com a figura 2. O pico máximo de absorção corresponde ao primeiro estado excitado de cada molécula na fase gasosa e esse estado é composto por uma transição eletrônica HOMO-LUMO (+80%) em todas as quatro moléculas conforme mostrado na figura 1.

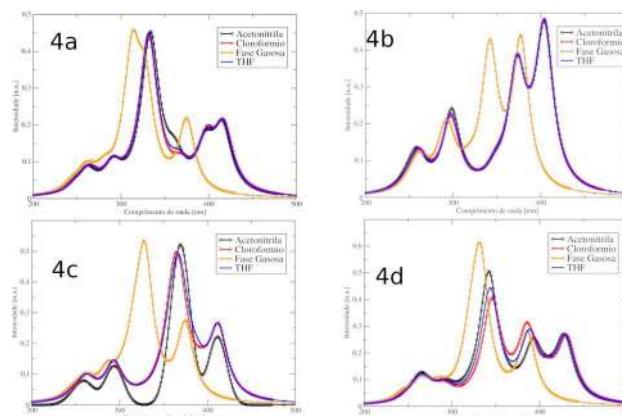


Figura 2: Espectro de absorção considerando 10 estados excitados para fase gasosa e solventes Acetonitrila, Clorofórmio e THF.

Conclusões

Em virtude dos cálculos teóricos realizados com os novos compostos de Difluoroboron β -dicetonatos Flavanonas destacamos as fortes características fotofísicas e propriedades ópticas com possíveis aplicações em dispositivos optoeletrônicos.

Agradecimentos

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Reposicionamento de fármacos utilizando triagem virtual baseada em ligante, com interesse ao tratamento da Doença de Chagas

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Palavras-Chave: proteassoma, Doença de Chagas, triagem virtual.

Introdução

As doenças tropicais negligenciadas são um subconjunto de doenças infecciosas conhecidas por serem prevalentes entre as populações mais pobres do mundo,¹ destacando-se o grupo de doenças cujos agentes etiológicos pertencem à família dos tripanossomatídeos, responsáveis pelas doença de Chagas, leishmaniose e tripanossomíase africana.² Com o surgimento do proteassoma como alvo biológico promissor,^{3,4} este trabalho propôs o uso de triagem virtual baseada em ligante para o reposicionamento de fármacos visando encontrar novos compostos para o tratamento da Doença de Chagas, utilizando as subunidades $\beta 4$ e $\beta 5$ proteassoma 20S de *Trypanosoma cruzi*, modelado por homologia comparativa como alvo biológico.

Metodologia

Para o LBVS (do inglês *Ligand-based Virtual Screening*) foram utilizadas três bases de dados de fármacos pré-aprovados em agências regulatórias: DrugBank, FDA e ZINC, previamente preparadas com o software OMEGA⁵ e, posteriormente, 'filtradas' com ROCS e EON (Open Eye),⁶ usando o composto **GSK3492454** como referência. Os compostos resultantes dessa triagem por similaridade (de forma e de eletrostática, com ROCS e EON) foram submetidos à análise toxicológica com o auxílio do software DEREK (*Deductive Estimate of Risk from Existing Know-edge*).⁷ A última etapa da triagem foi a realização das simulações de *docking*, analisando-se os valores de escore e as interações químicas dos fármacos com os resíduos do sítio ligante. Para o ensaio biológico, foram utilizadas as células LLCM-K2 infectadas com a forma amastigota da cepa Tulahuen LacZ de *T. cruzi*. O Benznidazol foi utilizado como controle interno nas mesmas concentrações dos compostos (controle positivo).

Discussão

A primeira etapa da triagem virtual foi realizada com o software ROCS e EON,⁶ selecionando-se os quinhentos compostos mais bem pontuados pelo índice de Tanimoto de cada base de dados. Esses compostos foram submetidos à análise toxicológica com o auxílio do software DEREK⁷, restando um total de 423 fármacos. A última etapa da triagem foi

a realização das simulações de *docking*, utilizando o modelo por homologia comparativa das subunidades $\beta 4$ e $\beta 5$ do proteassoma 20S de *Trypanosoma cruzi*. Os fármacos selecionados foram: Bepotastine besilate, fármaco **12** e Sorafenib.

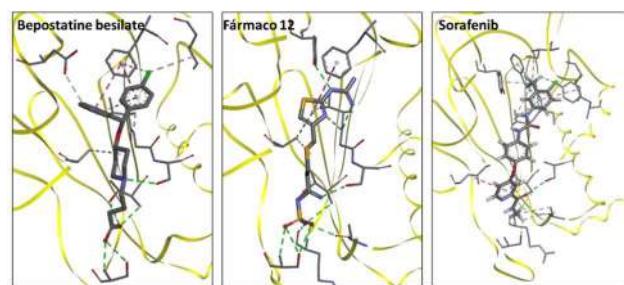


Figura 1. Poses de docking dos fármacos bepotastine besilate, fármaco **12** e Sorafenib,

O Sorafenibe obteve um IC_{50} abaixo de 10 μM . Entretanto, demonstrou alta toxicidade para a linhagem epitelial utilizada no ensaio. O fármaco **12** não se mostrou citotóxico ($EC_{50} < 300 \mu M$), mas obteve um alto valor de IC_{50} , de 221,8 μM , com um índice de seletividade de 6,35. O bepotastine besilate não eliminou as formas amastigotas que, ao final do ensaio, transformaram-se em tripomastigotas e lisaram as células.

Conclusão

O fármaco **12** apresentou o melhor resultado para eliminar as formas amastigotas de *T. cruzi*. Por não ser citotóxico na concentração mais alta utilizada no ensaio (250 μM), torna-se interessante a realização de novos ensaios biológicos aumentando-se a concentração do ensaio para entender melhor a dinâmica de atividade tripanocida do fármaco.

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<https://www.eyesopen.com> (b) OpenEye Scientific Software. EON 2.2.0.5. <https://www.eyesopen.com>

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Modeling the stabilizing effects in energetic materials of diphenyl-amine and curcumin

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The decomposition of energetic materials, especially propellants, generates nitrous gases and free acid nitrates. These compounds accelerate the rate of the acid-catalyzed decomposition reaction [1], an undesirable property. Therefore, in order to increase the shelf life of the material, certain additives called stabilizers are used [2].

Stabilizers can capture the acid nitrates by reacting with them [3] thereby forming more stable products [1]. A well-known stabilizer is the diphenyl-amine (DPA), but another promising alternative is curcumin [4], of IUPAC name (1E, 6E)-1,7-bis(4-hydroxy-3-methoxyphenyl)-hepta-1,6-dien-3,5-dione (FIG. 1).

To compare and evaluate the properties of DPA and curcumin as stabilizers of propellants, we investigated the possibility of electrophilic attacks.

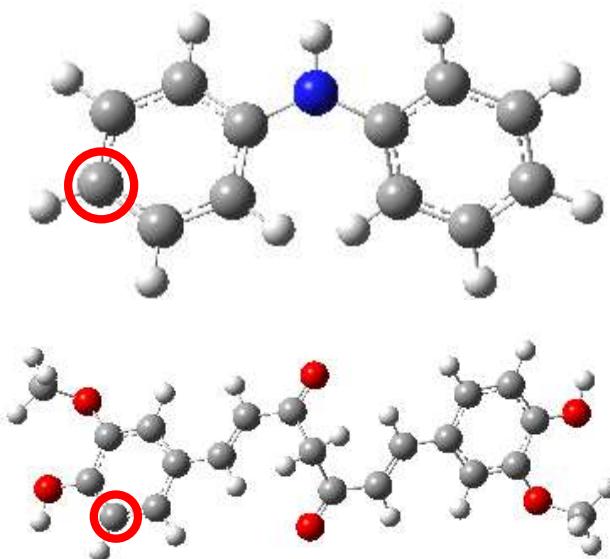


FIG. 1 – DPA (top) and Curcumin (bottom). Oxygen - red, nitrogen - blue, carbon - gray and hydrogen - white. The attacked carbons are circled in red.

The molecules were optimized using the DFT/B3LYP//6-31G(d) method implemented in Gaussian 09. For each molecule, a transition state describing the electrophilic attack by the nitronium ion (NO_2^+), corresponding to the capture of acid nitrate, was found.

The transition states agree with chemical intuition: directive effects of the substituents in the

aromatic rings and steric effects play a role. For DPA, the cation attacks the para position (para-DPA). For curcumin, it is the ortho substitution relative to the hydroxil substituent that is attacked by NO_2^+ . A transition state for each case was found and are shown in FIG. 2.

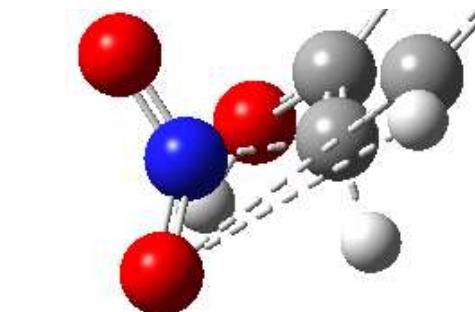
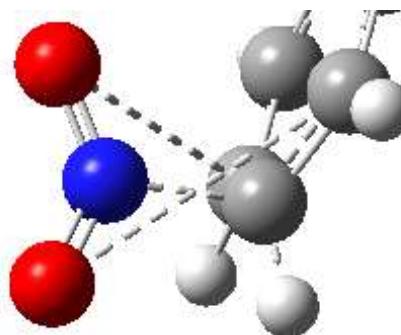


FIG. 2 –Transition state geometries for the nitronium ion attacks: DPA (top) and Curcumin (bottom).

Our results indicate that Curcumin is in fact a good alternative for DPA because it is more susceptible to the attack by a nitronium ion. This result is especially important considering that curcumin is one of the cheapest and most abundant known green stabilizers [5].

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Artificial photosynthesis: A theoretical approach about ruthenium catalysts.

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Keywords: Water splitting, DFT, Pourbaix.

Seeking to solve the energy and environmental issues, water splitting or artificial photosynthesis have shown to be a promising approach to decrease environmental damage derived from energy production and consumption.¹ Ruthenium complexes are the most successful homogeneous catalysts employed so far.² In our group, we have been working on the development of new catalysts for water oxidation and on the study of their reactions. In the present work we will show that theoretical calculations can be used to map the Pourbaix diagram of complexes as a means to understand their intricate pH-dependent electrochemistry observed in our experiments.

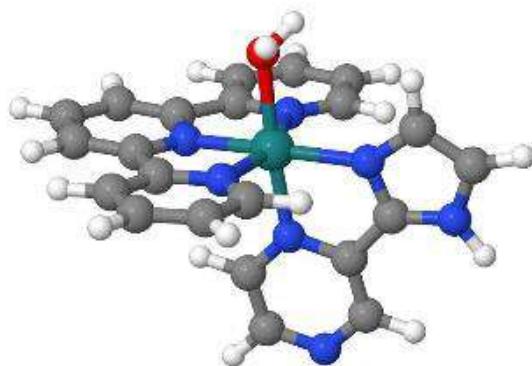


Figure 1 - Studied Complex

Theoretical studies were performed using the software ORCA³ (version 4.2.0), using PBE0⁴ hybrid functional and def2-svp⁵ basis set. The CPCM⁶ method was used. To obtain better results and speed up calculations, RIJCOSX approximations, grid 4, and Tightscf methods were employed. Avogadro software was used for structure visualization.⁷ The isodesmic methodology was employed in order to find pK_a and potential values.⁸

Pourbaix diagram is an important tool to understand water splitting. As a map of stability, it shows which species are stable in each potential and pH. Therefore, [Ru(OH₂)(tpy)(impz)]²⁺ (Fig. 1) had their Pourbaix Diagram proposed (Fig. 2).

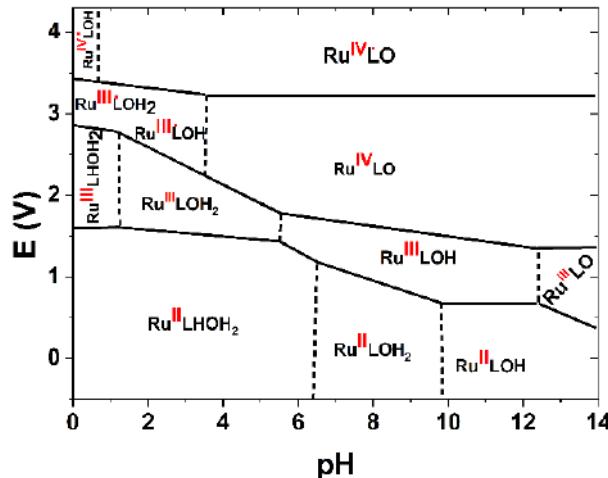


Figure 2 Theoretical Pourbaix diagram, which L = impz. Each dot above the letter L means oxidation.

This diagram shows the ligand as non-innocent and it is necessary to oxidize impz to achieve the highest oxidation state. Our calculations show that the Ru-O distance decreases when deprotonations occur. Moreover, deprotonations are correlated with the potential drop. In the literature, Ru(V) frequently appears as a catalytic species of water, however, in this case we found [Ru(IV)(O)(tpy)(L⁺)]²⁺ as a possible catalytically active species.

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Perfil energético e estrutural de reações tio-Michael entre derivados tio-enulosídicos e etanotiol

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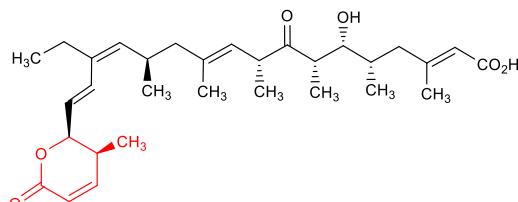
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Palavras-Chave: enulosídeos, adição tio-Michael, cálculos MP2.

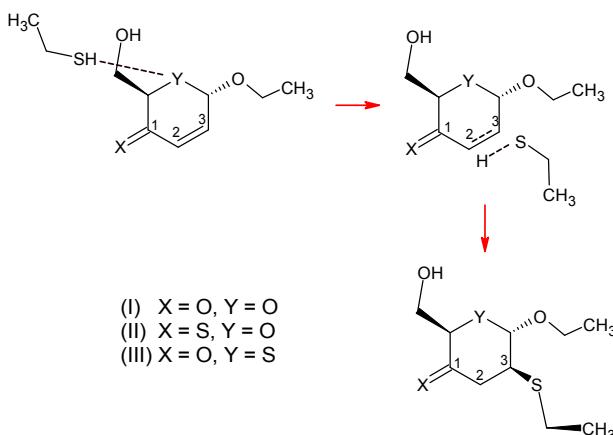
1 – Introdução

Acredita-se que a porção δ -lactona α,β -insaturada da leptomicina B (Esquema-1) é responsável por várias atividades biológicas [1] devido a possibilidade de se comportar como um acceptor tio-Michael de nucleófilos biológicos como, por exemplo, grupos sulfidrilas em resíduos do aminoácido cisteína.



Esquema 1 – Estrutura da leptomicina B.

A exemplo dos seus correspondentes compostos oxo, [2] derivados tio-enulosídicos obtidos por substituições nas posições X e Y (Esquema-2) são candidatos bioisôsteros da leptomicina B.



Esquema 2 – Adição tio-Michael entre o etanotiol e derivados enulosídicos.

Neste trabalho, os perfis cinético e termodinâmico da reação de adição do tipo tio-Michael foram estudados através de cálculos de estrutura eletrônica para os compostos I-III, utilizando o etanotiol como sistema modelo para representar a cisteína.

2- Metodologia

Cálculos de MP2/6-311++G(d,p) foram empregados para otimizar a estrutura dos reagente, produto e estado de transição (ET) para reação tio-Michael entre os compostos I-III e o etanotiol. Cálculos de frequência (1bar e 298,15 K) na aproximação harmônica foram realizados para o cálculo da energia livre e caracterização de reagentes, produtos e estados de transição (ET).

Os cálculos foram realizados com o programa Gaussian 09, empregando seus critérios internos padrões. Todos os cálculos foram realizados no Laboratório de Química Teórica e Computacional Manuel Braga.

3 – Resultados e discussões

Na Tabela 1 são apresentados os resultados da variação da energia livre de Gibbs.

Tabela 1 – Variação da energia livre de Gibbs para o ET (ΔG^\ddagger) e da reação ($\Delta_R G$).

Enulosídeo	ΔG^\ddagger (kcal mol ⁻¹)	$\Delta_R G$ (kcal mol ⁻¹)
I	75,1	-13,9
II	44,5	-11,2
III	47,2	-14,8

Os resultados da Tabela 1 indicam que a substituição de oxigênio por enxofre não modifica de maneira apreciável a energia de livre de Gibbs da reação, porém diminui expressivamente (41%) a barreira de energia para formação do produto. Essa diminuição deve-se, provavelmente, a maior estabilização do ET em II que em I, uma vez que a distância de C₃--S para as estruturas dos ET desses enulosídeos valem 1,924 Å e 2,001 Å, respectivamente. Outro resultado dos nossos cálculos diz respeito ao aumento do momento de dipolo elétrico entre a estrutura que representa o reagente e o estado de transição. Enquanto este aumento foi de 5,71 D para I, para II foi de 8,12 D. Estes valores apontam que essas reações de adição devem ser favorecidas em solventes mais polares.

4 – Referências

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Modo de Ligação entre a Proteína Dissulfeto Isomerase A1 e seu Oxidante Hidroperóxido de Urato – Um Estudo Computacional.

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Palavras-Chave: *Proteína Dissulfeto Isomerase, hidroperóxido de urato, docagem molecular.*

Introdução. A Proteína Dissulfeto Isomerase (PDI) é uma chaperona envolvida na oxidação, redução e isomerização que atua durante o enovelamento de proteínas. Sendo que suas funções biológicas são reguladas estritamente por seu estado redox². Sua estrutura é formada por quatro domínios tiorredoxina **a**, **a'**, **b** e **b'**, um conector **x** entre os domínios **b'** e **a'** e uma alfa-hélice c-terminal¹. Estudos experimentais demonstraram que a PDI é oxidada pelo hidroperóxido de urato (HOOU), um forte oxidante gerado através oxidação do urato. A curta meia vida do HOOU dificulta o entendimento da oxidação da PDI por essa espécie². Diante disso, empregou-se diversos métodos computacionais para compreender o modo de ligação entre essas duas espécies.

Metodologia. Utilizou-se a enzima PDI, código PDB: 4EKZ. Inicialmente foram feitas as correções e ajustes necessários na enzima, entre os quais o estado de protonação dos aminoácidos e a modelagem de regiões que não estavam resolvidas na estrutura cristalográfica. Em seguida realizou-se uma simulação de dinâmica molecular, utilizando o pacote GROMACS 5.1.4 para avaliar a estabilidade do modelo PDI. Desenhou-se todos os ligantes utilizando o ChemSketch freeware versão 12.01, otimizando-os com o campo de força CHARMM e posteriormente com B3LYP/6-311G ++ (d,p) usando o software Gaussian 09. Os enantiômeros **R** e **S** foram gerados nas formas tautoméricas N3, N7 e N9. As topologias foram geradas pelo servidor Acype, e as cargas atômicas calculadas pelo Hamiltoniano AM1-BCC. As simulações de docagem molecular foram realizadas com o AutoDock 4.3.2 utilizando a última conformação PDI da dinâmica. A detecção e caracterização da cavidade da PDI foi realizada usando o servidor ProteinPlus. No estudo de aromaticidade utilizou-se o método B3LYP/6-31G(d) para a otimização de geometria, enquanto os métodos de Índice de Flutuação Aromática (FLU), Modelo do Oscilador Hármonico de Aromaticidade (HOMA) e Índices Bird foram calculados usando o software Multiwfn 3.8. Por fim, a mutação Trp52Ala foi realizada utilizando a biblioteca de rotâmeros Dunbrack presente no Chimera 1.10.133, e submeteu-se o complexo hidroperóxido de urato/PDI mutada a simulações de dinâmica molecular.

Resultados. A dinâmica molecular mostrou uma estabilidade na flutuação do RMSD para a PDI após 2 ns e um RMSD final de 1,16 Å, valor comparável aos obtidos em estudos anteriores. Identificou-se uma nova cavidade entre os domínios **a** e **a'**. Estudos empregando cálculos DFT mostraram que a espécie RN7 do HOOU é a mais estável em solução, sendo utilizada nas simulações posteriores. A docagem do ligante RN7 mostrou três modos de ligação com a PDI. A dinâmica molecular dessas conformações indicou um tempo de residência de 11,69 ± 7,35 ns sugerindo se tratar de um oxidante mais seletivo e com um importante papel na sinalização redox. Além disso, a dinâmica molecular sugeriu uma interação de empilhamento π - π entre os anéis do hidroperóxido de urato e o grupo indol do Trp52, indicando que a perda de planaridade no HOOU não abole a aromaticidade desse oxidante. Os índices de aromaticidade HOMA, FLU e Bird mostraram que o HOOU possui uma aromaticidade residual. Já a mutação Trp52Ala mostrou um tempo de residência quatro vezes menor para o hidroperóxido de urato, indicando que este aminoácido é importante para à ligação e consequentemente para transferência de equivalentes oxidantes entre essas espécies redox.

Conclusão. O uso de diferentes métodos computacionais mostrou que o oxidante hidroperóxido de urato é reconhecido pelo sítio ativo da PDI de modo mais específico que outros oxidantes de baixo peso molecular.

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On the aromaticity of (BN)₃-pyrenes

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Keywords: pyrene, aromaticity, BN

Introduction

Graphene and its derived structures remain one of the hot topics in the research of new materials. One possibility of derivation are structures identified as polycyclic aromatic hydrocarbons (PAHs) that are promising systems for several applications. The pyrene belongs to this classification and is relevant in terms of optoelectronic properties¹. Following the trend of modifying these structures to obtain modulated properties and stability², the derivatives indicated in Figure 1 are analyzed in terms of aromaticity, which is a central property for organic compounds.

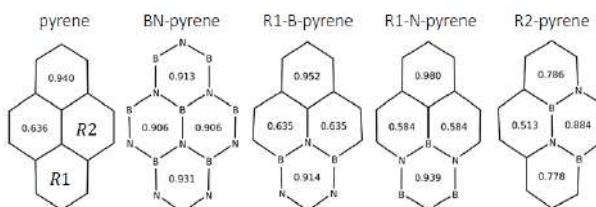


Figure 1. Selected isomers for analysis, with a nomenclature. The calculated HOMA index, obtained from the optimized geometry at CAM-B3LYP/def2-TZVP, is presented for every cycle of six atoms.

Methodology

First, optimization of geometry is performed using B3LYP and CAM-B3LYP functionals, with the def2-TZVP basis set. After checking the planarity of the structures, the HOMA index³ is calculated for every cycle. The ELF calculation⁴ also complements the analysis from a wave function point of view. Finally, NICS_T⁵ is applied to obtain information about the interaction with magnetic fields.

Results and Discussion

Figure 1 reveals that the BN rings increase the HOMA values for the rings in the system, the deformation on the geometry make the values get closer to one. The ELF_π shows a measure of the delocalization of the π electrons and agrees with HOMA results. Figure 2 shows the first bifurcation points, and they occur on the rings with the lowest HOMA values. Single point calculations for the triplet states were also carried out; in comparison with the pyrene, the derivatives increase the singlet-triplet splitting and the R2-pyrene is the only one that narrows the gap in ~0.5 eV.

Aromaticity, as a multidimensional property also deals with how the system interacts with an external magnetic field. NICS calculation can give insights into this behavior, particularly when isolating the contribution of π electrons. Figure 3 shows the result for two of the systems. The NICS scan shows

negative values for the chemical shift, which is characteristic of aromatic systems (strong diatropic induced current). The BN rings have subtler shifts for the out of plane component of the π electrons contribution when compared to CC rings.

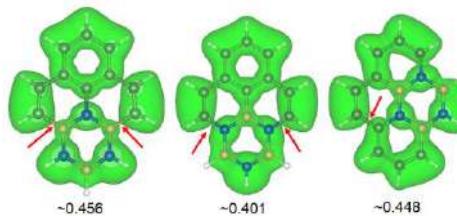


Figure 2. First bifurcation points of the ELF_π. The approximated value of the isosurface cutoff is presented for each system.

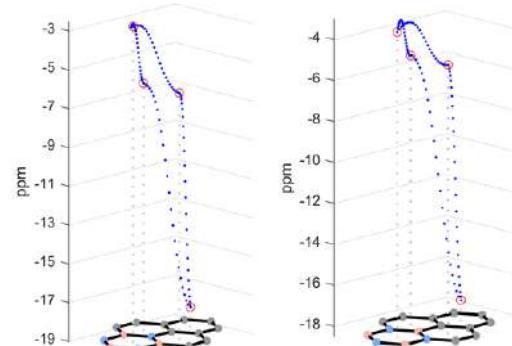


Figure 3. NICS(1.7)_{πzz} (in blue) for R1-pyrene variations, calculated at B3LYP/6-311+G(d,p). The set of dummy atoms forms a trajectory that connects the center of the rings.

Conclusion

The BN substitution seems to increase the stability of the pyrene framework as seen from the ST splitting increase. Beyond being isoelectronic to the CC pair, the BN adds to the system a degree of polarization and some change in the covalent character of the bonds. From a structural point of view, aromaticity is preserved or even enhanced.

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Comparison between mono- and decamer representations for ligand screening of MIPs using Classical Molecular Dynamics

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Keywords: molecularly imprinted polymers, molecular dynamics, biological template.

Abstract: Molecularly imprinted polymers (MIP) are ligand matrices with complementary cavities to target molecules, imprinted on their structure during polymerization [1]. Classical Molecular Dynamics (MD) is among the most used computational methodologies to aid ligand screening to achieve the best polymer for the selected template [2]. Since the non-covalent interactions that govern the non-covalent imprinting are dynamical and the solvent has an active role in the formation of the cavities, this many-body analytical approach to assist experiments is justified. However, even among the MD community there is no consensus about how the overall system should be modelled to better represent the real pre-cavities formation and properly increase the quality of the results [2]. To further improve MIP's ligand screening using MD, in this work we investigated the differences between mono and decamer representations of the ligands 2-vinylpyridine (2VP), acrylic acid (AAC) and 2-hydroxyethylmethacrylate (HEMA) with the Asian lineage Zika virus P31 epitope as template. The statistical sampling was done in NPT ensemble in three replicates of 100 ns each under 310 K and 1 bar. The all-atom OPLS force field [3] and LigParGen OPLS/CM1A web server [4] were used to obtain all molecular parameters. GROMACS 2019 [5] and VMD [6] were used for numerical integration and analysis. All simulations were done in a 6.3 CentOS computing cluster with up to 512 cores of 128 GB RAM each. Structural analyses of the template (RMSd and Rg_{xyz}) show better conformation stability using the decamer representation while the top 5 hydrogen bonding occupancy analysis shows that the decamer representation greatly accentuates the differences between the ligands. These findings indicate that, for the chosen template, a larger ligand oligomeric chain could increase the quality of the screening, leading to a better aid for the experimental synthesis.

	Rg _{xyz} [nm]	
	Monomer	Decamer
2VP	0.885 ± 0.058	0.745 ± 0.020
AAC	0.825 ± 0.039	0.758 ± 0.014
HEMA	0.832 ± 0.054	0.882 ± 0.044

	Top 5 Hydrogen bond Occupancy (%)		
	AAC	2VP	HEMA
Monomer representation			
8.35	7.03	4.50	
8.11	6.47	3.97	
6.61	3.05	5.40	
4.57	3.05	4.46	
4.50	2.28	4.09	
Decamer representation			
93.55	43.31	54.24	
91.85	21.35	29.67	
87.17	10.60	16.34	
83.85	10.12	12.66	
79.87	7.37	11.93	

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	RMSd [nm]	
	Monomer	Decamer
2VP	0.649 ± 0.079	0.537 ± 0.087
AAC	0.635 ± 0.073	0.404 ± 0.034
HEMA	0.610 ± 0.064	0.615 ± 0.063



A QSAR study of cannabinoids using the PLS method

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Keywords: cannabinoids, PLS, QSAR.

INTRODUCTION

Cannabinoid compounds present a wide therapeutic applicability, being able to act in the treatment of eating disorders, nausea, multiple sclerosis, anxiety and depression, for example [1]. However, the pharmacological use of these compounds is controversial and not well accepted due to the difficulty of isolating the psychotropic effects caused by them. The receptors that bind cannabinoid compounds are CB1 (which is found mostly in the central nervous system and in large quantities in the brain) [2] and CB2 (which is found in the peripheral nervous system) [3].

A series of cannabinoid compounds were selected from the literature so that QSAR (Quantitative Structure-Activity Relationship) models could be generated to predict the biological activity of cannabinoid compounds in order to suggest new cannabinoid compounds that could simultaneously act in a therapeutic way and do not present psychotropic effects.

METHODOLOGY

Gaussian 09 software was used to perform optimization and frequency calculations on the cannabinoid compounds, employed by Density Function Theory B3LYP method with 6-31G++(d,p) basis set. Dragon software generated molecular descriptors. An initial selection of the descriptors was done by correlation coefficients between descriptors and biological activity. Then, through genetic algorithm analysis (BuildQSAR software), the most relevant descriptors were selected. PLS (Partial Least Square) analysis were performed by Pirouette software and two PLS models were generated: PLS-CB1 and PLS-CB2, which describes the relationship between the structure of cannabinoid compounds with the biological activity values presented for CB1 and CB2 receptors, respectively. Additional validation tests were done on QSARModeling software.

RESULTS

Values of $q^2 > 0.5$ and $r^2 > 0.6$ are considered satisfactory for PLS models [4,5]. For PLS-CB1 model, molecular descriptors E3p (3rd component accessibility directional WHIM index/ weighted by polarizability), R6e+ (R maximal autocorrelation of lag 6 / weighted by Sanderson electronegativity), Jhete (R maximal autocorrelation of lag 6 / weighted by Sanderson electronegativity), ATS6v (R maximal

autocorrelation of lag 6 / weighted by Sanderson electronegativity), R6u (R maximal autocorrelation of lag 6 / weighted by Sanderson electronegativity), H5m (R maximal autocorrelation of lag 6 / weighted by Sanderson electronegativity) and nRORPh (R maximal autocorrelation of lag 6 / weighted by Sanderson electronegativity) were selected resulting in an acceptable PLS model ($r^2 = 0,685$, $q^2 = 0,609$ and $r^2_{test} = 0,769$; Figure 1a).

For PLS-CB2 model, molecular descriptors ATS6v, R5v+(R maximal autocorrelation of lag 6 / weighted by Sanderson electronegativity), JGI2 (R maximal autocorrelation of lag 6 / weighted by Sanderson electronegativity), Hy (R maximal autocorrelation of lag 6 / weighted by Sanderson electronegativity), MATS7p (Moran autocorrelation of lag 6 weighted by polarizability), Jhete and MATS6e (Moran autocorrelation of lag 6 weighted by Sanderson electronegativity) were selected resulting in an acceptable PLS model as well ($r^2 = 0,825$, $q^2 = 0,771$ and $r^2_{test} = 0,845$; Figure 1b).

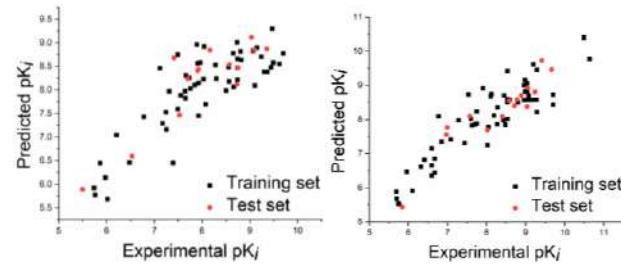


Figure 1. Biological activity prediction by (a) PLS-CB1 and (b) PLS-CB2.

CONCLUSION

The validation tests showed for both PLS-CB1 and PLS-CB2 models are robust and were not obtained by chance correlation. Through the mathematical models obtained by PLS method, it was showed that they were able to predict the biological activity of the cannabinoid compounds.

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Mechanistic Aspects of the Photophysics of Nature-inspired UVA Filters Based on Meldrum Derivatives

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Keywords: Natural sunscreen, Excited state dynamics, Meldrum derivatives.

INTRODUCTION: Skin photoprotection against UV-A radiation is crucial, but it is hindered by the sparsity of approved commercial UV-A filters. Sinapoyl malate (SM) derivatives are promising candidates for a new class of UV-A filters.¹ They have been previously identified as efficient photoprotective sunscreen in plants due to their fast nonradiative energy dissipation. In this work, we investigate the photodynamics of two new SM derivatives (Figure 1), coumaryl Meldrum (CMe) and sinapoyl Meldrum (SMe).^{2,3} Both were designed for application as UV-A filters, aiming at maximizing their long-term photostability upon irradiation and efficient nonradiative decay.

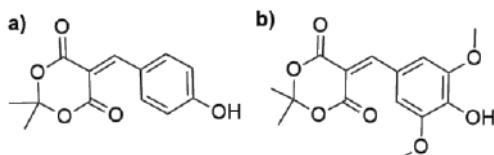


Figure 1: Molecular structure of a) Coumaryl Meldrum (CMe) and b) Sinapoyl Meldrum (SMe).

METHODOLOGY: Geometry optimizations of the ground and excited states and linear interpolations in internal coordinates (LIIC) were done at (TD)DFT level using ω B97XD/cc-pVDZ and PCM/Ethanol. Excitation energies were computed at ω B97XD/aug-cc-pVTZ and MS-CASPT2/ANO-L-VDZP levels. Excited-state dynamics and spectrum simulations were done at TD- ω B97XD/cc-pVDZ (PCM/Ethanol) level using the Newton-X program.

RESULTS: Supported by experimental data, our theoretical approach encompasses the characterization of the potential energy surfaces (PES) and excited-state dynamics simulations of CMe and SMe. Their photodynamics is schematically illustrated in Figure 2. Upon photoexcitation to the bright S_1 state, the population evolves in a sub-ps scale (τ_{CT}) towards a $\sim 90^\circ$ twisted minimum around the allylic double bond. This minimum has a twisted intramolecular excited state (TICT) character and is located 0.2 eV below an S_1/S_0 minimum energy crossing point (MECP). The sloped intersection enables a fast (τ_{IC} equals 0.6 ps for CMe and 1.2 ps for SMe) and efficient nonadiabatic transition, regenerating the S_0 state after vibrational cooling (τ_{VC}). An additional minimum, with a locally excited

(LE) character, was located for SMe and accounts for the weak fluorescence and slower nonradiative decay observed for this molecule. Sigmoid functions can nicely fit the excited-state populations, meaning that the dynamics follows a two-step logistic-decay, characterized by the population of an excited-state intermediate species (TICT), followed by an internal conversion from this intermediate.

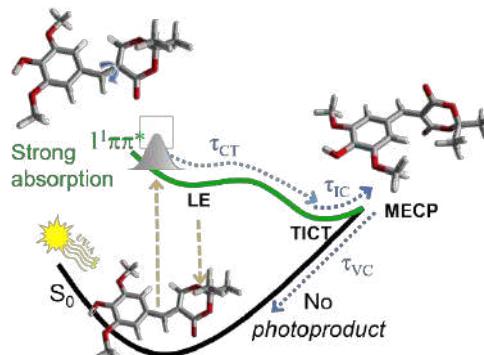


Figure 2. Schematic topography of the PES for SMe.

CONCLUSIONS: Using reaction pathways and excited-state dynamics simulations, we could elucidate the photodeactivation mechanism of CMe and SMe. Both molecules show an ultrafast decay pathway and internal conversion lifetimes in excellent agreement with the experiments, especially for CMe. Our theoretical analysis allied with the experimental results has shown that CMe and SMe are outstanding candidates for UVA filters in sunscreen formulations.

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Starting Structures of Lanthanoid Complexes with Stereochemical Control for Molecular Modeling

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Palavras-Chave: *Lanthanide Complexes, Stereoisomerism, Coordination Chirality.*

Introduction

A new algorithm to generate starting structures of lanthanoid complexes, with full stereochemical control, chirality recognition, and stereoisomer identification is advanced. Indeed, most of the attempts to get a good starting structure for computational chemistry calculations do not consider the combinatorial explosion of different conceivable stereoisomers inherent to metal complexes of higher coordination numbers. The algorithm solves this problem, and has been implemented in a software which can be freely downloaded (<https://complexbuild.sparkle.pro.br>).

Methodology

The implementation consists of two big sections: a frontend part, which takes as input values certain complex coordination characteristics, such as the metal ion, the ligands, the polyhedral shape, and the stereoisomer permutation; and a backend section, that calculates starting structures for the complex. Calculations of all possible stereoisomers can also be done. The Complex Build software contains more than 15.000 lines of Python programming language codes, besides the auxiliary multifunctional packages NumPy, SciPy, Pandas, Tkinter, Matplotlib, and others.

Results and Discussion

As an example, let us consider the lanthanide complex of generic formula $M(AB)_4$, of CSD (Cambridge Structural Database) refcode CIRKET, of coordination number 8, shape TDD-8 (triangular dodecahedron), and formula $[Eu(TTA)_4]$ where TTA stands for 4,4,4-trifluoro-1-(2'-thienyl)-1,3-butanedione. In principle, there are 51 possible stereoisomers for this complex¹: 44 of these being chiral (including the crystallographic one) that form 22 enantiomeric pairs, while the other 7 are achiral. These isomers are grouped into 7 different subsets (see Table 1), each one with a distinct coordination polyhedron point-group symmetry, i.e.: C_1 , C_2 , C_s , S_4 , D_2 , C_{2v} , D_{2d} .

Figure 1 shows one of the converged geometries for this complex. Complex Build is also capable of calculating each of the conceivable stereoisomers, as well and to save them as input files ready to be submitted to other molecular modeling softwares for further calculations, such as

MOPAC, LUMPAC, Gamess, ORCA, Gaussian, and several others.

Table 1: Number of possible stereoisomers and enantiomeric pairs for each coordination point-group in the $[Eu(TTA)_4]$ complex of shape TDD-8.

Point-group	Number of stereoisomers	Chirality	Number of Enantiomeric pairs
C_1	22	Yes	11
C_2	18	Yes	9
C_s	2	No	-
S_4	4	No	2
D_2	2	Yes	-
C_{2v}	2	No	-
D_{2d}	1	No	-

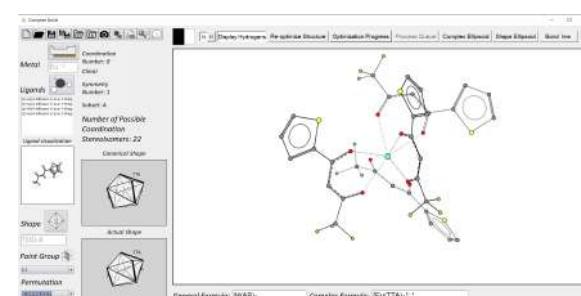


Figure 1: Complex Build main screen after construction of europium complex CIRKET.

Conclusions

We have developed in this work a new methodology to generate starting structures of lanthanoid complexes for further molecular modeling calculations that take into account their stereoisomerism, including chirality such as coordination polyhedron shape, point group and permutation. Complex Build focuses primarily on lanthanoid complexes; coordination compounds that display high coordination numbers, with a lack of ligand directionality that renders a large number of polyhedral shapes possible and with a largely unnoticed geometrical complexity, including chirality.

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An Uncomplicated but Effective Force Field for the Pre-optimization of Geometries of Metal Complexes for Quantum Chemical Calculations

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Keywords: Lanthanide complexes, Coordination stereoisomerism, Coordination chirality.

Introduction

The theoretical treatment of metal complexes requires starting structures as inputs for further sophisticated quantum chemical calculations. However, providing these input structures is no trivial matter; not only because the structures themselves are difficult to assemble, but also due to the large amount of conceivable coordination stereoisomers. To address this problem, we advance an algorithm to initialize and pre-optimize structures of metal complexes using an uncomplicated but effective force field with a reduced number of degrees of freedom to reliably generate starting structures of metal complexes with controlled stereochemistry, including chirality. Indeed, even a simple complex, such as the triaquatrinitro-Lu(III), of generic formula $\text{Ma}_3(\text{AA})_3$, of shape MFF-9 (muffin), already has 232 possible coordination stereoisomers, split between 10 achiral ones, and 111 pairs of enantiomers.¹

Truly, there are many difficulties involved in assembling hundreds of stereoisomers, with a guarantee of geometric completeness, in a reliable and exhaustive manner as good starting geometries for further computational chemistry calculations, such as those available in MOPAC, Gaussian and GAMESS. Hence, the need for automating the task. This is the basic motivation behind the Complex Build algorithm, fully implemented in the Complex Build software (<https://complexbuild.sparkle.pro.br>).

Algorithm Description

The algorithm forms the computational kernel of the Complex Build software, and requires, as input data, the set of ligands, a metal ion and (optionally) the shape of the coordination polyhedron and the corresponding stereoisomer permutation.

The algorithm relies on a few important pillars to work. The first is the uncomplicated force-field potential we call crowding. The crowding of a metal complex is split into two parcels: The coordination warp and the sterical congestion. The coordination warp quantifies how distorted the coordination system is when compared with a standard form. If the complex has a finite shape, the warp quantifies how much the coordination polyhedron is distorted. When the shape of the

complex is undefined and free, then it quantifies how stretched or compressed the coordinate bonds are. The steric congestion, on the other hand, is a repulsive-only potential that sums up the inverse of the distances between every pair of atoms in the molecule. These distances are weighted such that distances involving hydrogen atoms have less impact in the overall crowding. Essentially, the congestion is constantly trying to pull the complex apart and the warp is holding it together such that the coordination system remains undeformed.

The second pillar is the set of degrees of freedom (DoFs) that are accessible to the system for representing a particular geometry. The algorithm has five sets of ligand-accessible DoFs that can be used in each run. The first set contains the wheel and hinge angles. The wheel angle is the angle around the axis that contains the metal center and the tooth of a monodentate ligand, whereas the hinge angle is the angle around the axis that contains the two teeth of a bidentate ligand. The second set of DoFs are the coordination rays that allow a ligand to translate along the ray that contains its barycenter and the metal center. The third set of DoFs are the Euler angles, which allow a ligand to rotate around its own barycenter. The fourth set of ligand-accessible DoFs is the position vector of the ligand's barycenter in the coordination sphere, expressed in spherical coordinates. The last set of degrees of freedom accessible to the ligands are the internal torsions around sigma bonds.

Conclusion

The ComplexBuild algorithm is capable of assembling good starting geometries, even for rather complicated metal complexes of high coordination numbers. Once fully optimized with further quantum chemistry methods, the obtained final geometries are almost always true minima, without negative force constants.

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DECIPHERING THE ROLE OF THE C₇₀ NANOFLESH ON CHEMICAL REACTIVITY OF ATOMIC NITROGEN BY CAR-PARRINELLO MOLECULAR DYNAMICS

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keywords: molecular dynamics, Car-Parrinello, nanoflask.

INTRODUCTION

In recent years, research on fullerenes that encapsulate different chemical species has grown significantly. Morinaka *et al.* investigated the chemical reactivity of atomic nitrogen using a C₇₀ fullerene as a nanoflask (endohedral fullerene)¹. This work presents the analysis of these results using Car-Parrinello molecular dynamics (DMCP)².

METHODS

The structural data of the molecules were taken to the CPMD³ computational chemistry program, which carried out the simulation of the molecular dynamics of Car-Parrinello. Full geometrical optimization and total energy calculations were performed with the PBE functional, to maintain an adiabatic system, one μ fictitious mass of 400 u.a. was used, which proved effective during the whole simulation. To reduce the calculation for the electronic subsystem, the pseudopotential ultrasoft Vanderbilt, together with plane waves, was used. The temperature of the ionic subsystem was kept constant using the Nosé-Hoover thermostats at 300 K. The nitrogen atom was simulated in an electronically excited state N(²D), and in the ground state N(⁴S), and both were reactant with the hydrogen molecule (H₂).

RESULTS AND DISCUSSIONS

In Figure 1, the atomic interactions are shown for the nitrogen atom, in the ground state N(⁴S), with the hydrogen molecule and in Figure 2, the atomic interactions for the nitrogen atom, in the first excited state N(²D), with the hydrogen molecule, in order to identify and analyze the formation of the NH₂ radical.

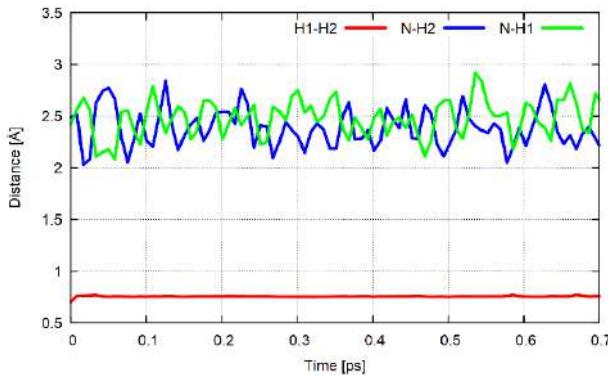


Figure 1. Bonding distance between the nitrogen atom N(⁴S) and the hydrogen molecule (H₂) during the simulation.

Through, the isosurfaces produced by RDG (reduced density gradient), in Figure 3, it is possible to observe the strong interaction between nitrogen N(²D) and

hydrogen atoms.

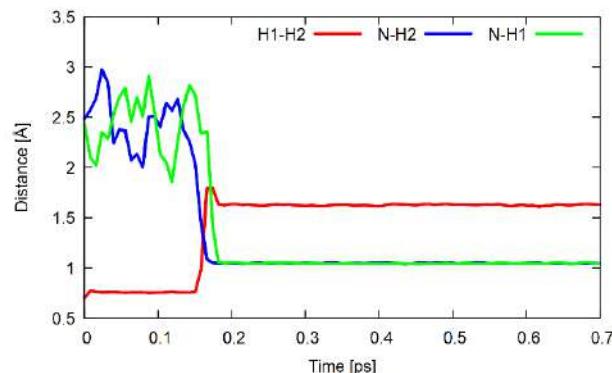


Figure 2. Bonding distance between the nitrogen atom N(²D) and the hydrogen molecule (H₂) during the simulation.

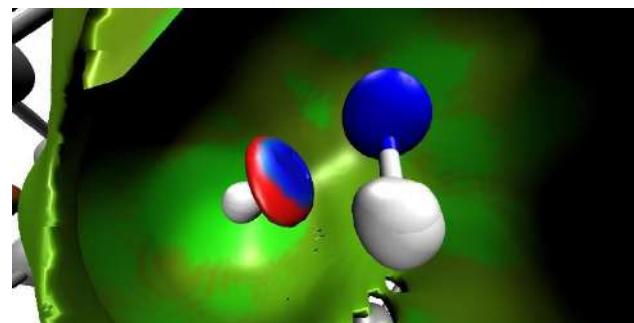


Figure 3. RDG isosurfaces for the nitrogen atom N(²D) and the hydrogen atoms inside a fullerene C₇₀. Strong attraction (blue), Van der Waals interaction (green) and strong repulsion (red).

CONCLUSIONS

It was confirmed through DMCP and RDG that the nitrogen atom in the ground state does not react with the hydrogen molecule at a temperature of 300K, inside the C₇₀ fullerene, as reported through experimental data by Morinaka *et al.* For the nitrogen atom in the first excited state, the formation of the NH₂ radical was observed.

ACKNOWLEDGMENTS

The authors are grateful for the support given by UEG.

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ESTUDO TEÓRICO ENTRE PESTICIDAS ORGANOFSFORADOS E ORGANOFSFOTIOATOS E A ENZIMA ACETILCOLINESTERASE HUMANA (HssAChE)

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Palavras-Chave: Docking, Dinâmica Molecular Acetylcolinesterase Humana, Organofosforados

INTRODUÇÃO

Os pesticidas são eficazes no controle de pragas, mas ao mesmo tempo, provocam graves problemas ambientais e para a saúde humana, pois apresentam alta toxicidade.¹ De acordo com a literatura, a toxicidade dos pesticidas organofosforados (OP) é aumentada quando ocorrem reações de dessulfuração metabólica oxidativa, onde a ligação P=S é transformada em uma ligação P=O.² Baseado neste contexto, o objetivo deste trabalho é estudar o modo de interação de diferentes pesticidas organofosforados (com ligações P=S e P=O) com a enzima Acetilcolinesterase humana (*HssAChE*), avaliar os parâmetros farmacocinéticos e o mecanismo de reação entre a enzima e os compostos.

MÉTODOS E RESULTADOS

As estruturas tridimensionais dos compostos OP (Figura 1) foram construídas por meio do programa Gaussview e suas cargas parciais atômicas foram calculadas utilizando o método B3LYP/6-31G. Após a construção das estruturas 3D dos OP, eles foram transferidos para o programa Molegro Virtual Docker, onde cada composto foi ancorado no sítio ativo da enzima *HssAChE* (código PDB 5HF9; resolução = 2.20 Å; inibidor = paraoxon). Os cálculos de dinâmica molecular foram feitos no Gromacs.

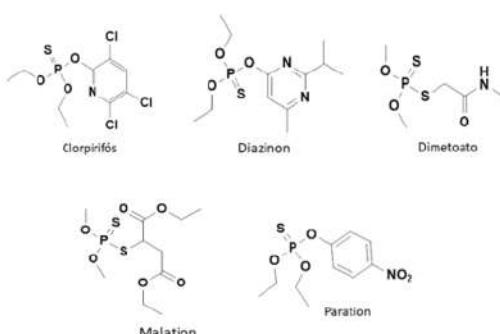


Figura 1: Estruturas dos OP.

Tabela 1: Valores da energia de interação intermolecular (kcal mol⁻¹) proteína/compostos obtidos do ancoramento molecular.

Compostos	Energia intermolecular	*Tox. (DL ₅₀ , mol kg ⁻¹)
Clorpirifós (P=S) e (P=O)	-27,86/-72,48	3,87/4,14
Diazinon (P=S) e (P=O)	-28,21/-71,59	3,08/3,08
Dimetoato (P=S) e (P=O)	-31,06/-48,44	3,08/3,07
Malation (P=S) e (P=O)	-29,29/-37,02	3,46/3,41
Paration (P=S) e (P=O)	-44,75/-76,22	2,81/2,88

*Resultados teóricos obtidos do ADMET.

Com os estudos de ancoramento molecular (Tabela 1), foi possível observar que os OP com ligação P=O apresentaram energia de interação intermolecular mais estável no sítio ativo da enzima quando comparados aos OP com ligação P=S, corroborando com os resultados apontados pela literatura. A maior estabilidade dos OP com P=O no sítio ativo da enzima pode ser explicado pelo fato do oxigênio aumentar o número de ligações de hidrogênio no sítio ativo da enzima.

CONCLUSÃO

Essa investigação teórica pode ser utilizada para direcionar o desenvolvimento de novas drogas a base de fósforo, contribuindo assim, para o tratamento de doenças neurodegenerativas.

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QUANTIFYING BOND STRENGTHS VIA A COULOMBIC FORCE MODEL: APPLICATION TO THE IMPACT SENSITIVITY OF NITROBENZENICS, NITROAZOLES AND NON-AROMATIC NITRAMINES MOLECULES

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Palavras-Chave. Bond Strengths, Coulombic Bonding Model, Impact Sensitivity

INTRODUCTION

The interatomic bond is a very useful concept in chemistry. Accurate theoretical calculations can provide insights into the nature and properties of different types of bonds¹. In this regard, to quantify the sensitivity of explosives, some authors quantify the sensitivities of energetic materials employing the bond dissociation energy (BDE) of the weak chemical bonds known as “trigger linkages”.

In this work, we developed models of sensitivity measured by h_{50} values based on a proposed Coulombic bonding model² that employs the distributed multipole analysis (DMA)³ charges to compute bond strengths of the N-NO₂ and C-NO₂ trigger linkages of 0 nitramines, 11 nitroazoles and 19 nitrobenzenic molecules.

METHODOLOGY

The geometries of all molecules were optimized with the DFT/B3LYP//6-311+G(d) method⁸⁷⁻⁸⁹ employing Gaussian 03. For the nitrobenzene molecules, single point DFT/B3LYP//6-311+G(d) calculations were performed on the (M06-2X)/TZVP geometries.

We considered the trigger linkages as Coulombic interactions between atoms and the DMA charge of each atom were obtained using the GDMA²⁴ program.

We defined the normalized weakest N-NO₂ and C-NO₂ Coulombic force, F_{nw} , as the weakest force in a molecule, according to the following expressions:

$$F_{nw} = \frac{F}{[\#CNO_2]^2}$$

$$F_{nw} = \frac{F}{[\#NNO_2]^2}$$

where F is the Coulombic force between atoms charges (monopoles).

RESULTS

RESULTS Plot of experimental h_{50} values vs. F_{nw} for each explosive molecule generated the different theoretical models to determine impact sensitivities (Figure 1).

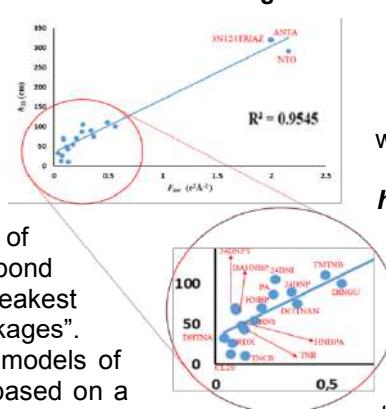


Figure 1 Plot of experimental h_{50} values vs. F_{nw} for each explosive molecule.

A linear model for the sensitivity was then derived as shown in Figure 1:

$$h_{50} = 135.35F_{nw} + 33.613$$

CONCLUSIONS

We found a very good correlation between the weakest normalized force (F_{nw}) and the respective h_{50} value of each molecule. The mathematical model proposed are sufficiently broad to predict the sensitivity values of the three explosive families considered simultaneously. Its application to the total set of 40 molecules led to predicted h_{50} values mostly small relative deviations.

To summarize. In this work, we proposed a general model to compute bond strengths from a Coulombic model having as input the DMA charge (monopole) values. This model was employed successfully to describe the impact sensitivity of explosives composed of molecules from three different chemical families, which shows its generality. Other applications of this force model to different chemical phenomena are under way.

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Adsorção do ácido fórmico catalisado por superfícies de cobre

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Palavras-Chave: Superfície Cu, adsorção de HCOOH, DFT

Introdução:

A desidrogenação do ácido fórmico (AF) em H₂ e em CO₂ (eq. 1) em superfícies metálicas é considerada uma reação com potencial de atender o aumento da demanda de energia. Trata-se de um substrato interessante, pois além de ser fácil e seguro de ser manuseado, o ácido fórmico é biodegradável e pode ser obtido de biomassa ligninocelulósica.^{1,2}



É de interesse deste trabalho estudar como o ácido fórmico reage nas superfícies (100) e (111) e em suas formas defeituosas. Os cálculos foram realizados no programa *Quantum Espresso*, utilizando o funcional de troca e correlação PW91, o pseudopotencial ultrasoft e ondas planas. A energia de corte das ondas planas e a malha de pontos K que melhor descrevem cada superfície foram otimizadas de forma a garantir uma convergência na energia de 10⁻³ Ry.

O intuito do trabalho é entender melhor a etapa fundamental de adsorção do ácido fórmico, a influência dos defeitos na adsorção bem como as etapas fundamentais de decomposição desse substrato.

Resultados e discussão:

Após a otimização do bulk, foi possível realizar os cálculos para otimizar ambas as superfícies. Para a superfície de cobre (100), utilizou-se uma energia de corte de 40 Ry, enquanto que na superfície(111), a energia de corte utilizada foi de 35 Ry. Na superfície (100), a malha de pontos k utilizada foi de 4x4x1, enquanto que na superfície (111) a malha utilizada foi de 3x3x1.

Na figura 1 verifica-se as duas estruturas de cobre utilizadas para as adsorções do ácido fórmico, após a realização do cálculo de otimização.

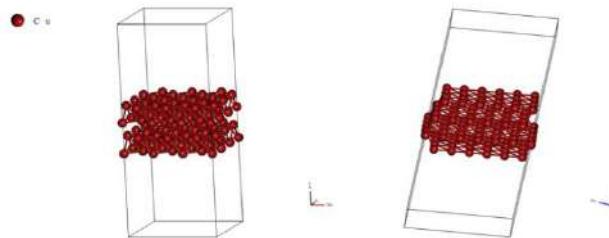


Figura 1: Superfícies de cobre (100) e (111)

Como o mecanismo de desidrogenação nas superfícies de cobre ainda é pouco conhecido, as adsorções serão feitas de várias maneiras, alterando os átomos em contato com a superfície, alterando a posição do ácido fórmico em relação a superfície e adsorvendo a molécula de HCOOH em diferentes posições nas superfícies.

Após o melhor compreendimento desse mecanismo, os próximos passos serão realizar alguns métodos para aumentar a energia de adsorção do HCOOH nas superfícies de cobre, como adicionar um outro átomo à superfície e variar a temperatura do meio.

Considerações Finais:

É possível, através dos cálculos DFT, simular as superfícies de cobre e com os estudos de adsorção, serão capazes de mostrar os principais sítios de interação do ácido fórmico com as superfícies de cobre.

Agradecimentos:

CNPq, CAPES, FAPEMIG, RenovaMin, INCT-ACQUA.

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Docking studies of naphthoquinones against SARS-CoV-2 main protease

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Keywords: Virtual screening, docking, SARS-CoV-2.

Introduction

Since the beginning of the SARS-CoV-2 disease pandemic, denominated COVID-19, the pharmaceutical industry has invested in modern and innovative research strategies to accelerate the release of new drugs to the market. The main strategies employ bioinformatics methods.

The molecular docking approach applied to a library of ligands against specific molecular targets, is known as virtual screening (VS) based on the receptor structure.

The VS process became widespread with the implementation of compound libraries, such as ZINC15, which is a bank with millions of commercially available molecules, prepared for experiments *in silico*.

These databases motivate the creation of a database of COVID-19 molecular targets prepared for VS, which can be used for the rational drug design.

This work also aims to evaluate by VS a series of approximately 100 naphthoquinones available to our research group for future experimental tests.

Methodology and results

Initially, the structure of SARS-CoV-2 main protease (PDB ID: 6W79) was selected and obtained from the Protein Data Bank (PDB - <https://www.rcsb.org/>). The crystallographic ligand-receptor complex was prepared and refined by energy minimization using the Chimera software [1].

Using the softwares Autodock Vina [2], through MolAr [3], the redocking of the complex was performed, obtaining a root-mean-square deviation (RMSD) value of 1.1688 Å.

The receiver operating characteristic (ROC) curve was also constructed using decoys generated by the online platform DUD-E (<http://dude.docking.org/>), and the area under the curve obtained was 0.9216.

Then, VS experiments were carried out using MolAr [3] with several naphthoquinones, having as an example, and one of the best placed, atovaquone (Figure 1).

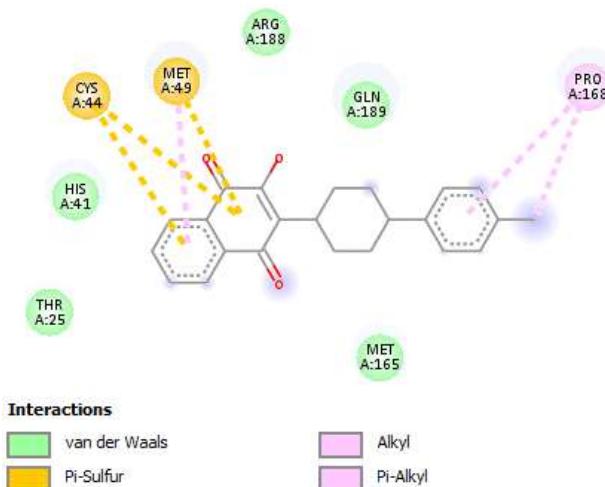


Figure 1. Interactions between the best pose generated for atovaquone and the 6W79 molecular target.

Conclusions

Through these experiments, it was possible to identify naphthoquinones with score values against the main protease of SARS-CoV-2 close to those of crystallographic ligands, using atovaquone as an example. The preparation of new targets and the inclusion of ligands are in progress, and these results will be followed by experimental tests.

Acknowledgments

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Cálculo do Tunelamento em Potenciais de Duplo Poço através dos Parâmetros da Barreira

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Palavras-Chave: Quantum Tunneling, Double Well Potential, Ammonia.

INTRODUÇÃO

A capacidade de partículas, ou sistema de partículas, de atravessar uma região do espaço cuja energia é maior que a energia da partícula é chamada de Tunelamento Quântico (TQ). Tal comportamento é impossível de acordo com a Mecânica Clássica. Na Química, esse efeito se coloca como a chance de elétrons, núcleos e átomos de tunelarem por uma região não permitida classicamente.

No caso de potenciais de duplo poço (PDP), o tunelamento é amplificado por uma espécie ressonância, causada pela interação entre as funções de onda centradas em cada poço. O objetivo do trabalho é o desenvolvimento de um método *ab initio* para o cálculo do TQ em PDPs partindo-se apenas da altura e da largura da barreira, as quais podem ser facilmente calculadas através de softwares comerciais ou obtidas experimentalmente. A grande vantagem do uso apenas desses parâmetros é a possibilidade da aplicação em sistemas grandes, como proteínas.

METODOLOGIA

Os métodos teóricos para a obtenção da frequência de tunelamento por segundo foram publicados pelo grupo em outro trabalho, no qual são extensivamente discutidos.¹ Parte-se do potencial trigonométrico simétrico:

$$U(y) = h \tan^2 y + b \sin^2 y$$

onde h e b são parâmetros de ajuste. Estes são obtidos através de um algoritmo, chamado ajuste ao tamanho da barreira (ATB), que modifica o potencial para que tenha a mesma altura e largura da barreira do PDP. A frequência de tunelamento é obtida através da fórmula:

$$\epsilon = \lambda_{m(q+m)}(\sqrt{b}) + \frac{1}{2} - b - m^2$$

onde λ é o set de autovalores associados a função esferoidal prolada angular (EPA) e $m = \sqrt{h + 1/4}$. O cálculo dos autovalores das funções EPA está implementado no software *Mathematica*.

Foram estudadas as moléculas NH₃, ND₃ e tropolone. A altura da barreira foi gerada através de cálculos utilizando o método CBS-QB3, para o estado fundamental e estado de transição, utilizando o software Gaussian09. A largura da barreira foi aproximada como a distância entre o

plano dos átomos H para NH₃ e ND₃ e como a distância entre os átomos H e O para o tropolone.

RESULTADOS

Os resultados dos cálculos encontram-se na Tabela 1, comparados com os resultados para o método de regressão partindo das coordenadas intrínsecas de reação (IRC).¹ Pode-se ver que os resultados para NH₃ e ND₃ de ambos os métodos estão em excelente concordância com o experimental. Já para o tropolone, o ATB gera valores mais acurados que o IRC.

Tabela 1: Valores para as frequências de tunelamento (10^8 cm^{-1}) para as moléculas estudadas e seus valores experimentais.^{1,2}

Molécula	IRC	ATB	Experimental
NH ₃	256	221	238
ND ₃	14,0	11,7	15,9
Tropolone	662	193	292

Os resultados podem ser melhorados com o refinamento das coordenadas de reação. Isso porque as variações nos valores das frequências de tunelamento para a molécula tropolone se devem a distorções causadas na largura da barreira pelo movimento de átomos não modelados, como átomos pesados. Essa mesma questão foi encontrada quando foram testadas moléculas mais complexas, como aminas substituídas.

CONCLUSÕES

O método se mostrou preciso desde que as coordenadas de reação sejam capazes de modelar o sistema durante o tunelamento. Ao contrário do tropolone, o movimento da amônia é simétrico, e por isso pode ser modelado por coordenadas simples. O trabalho ainda está em andamento e a perspectiva é introduzir coordenadas de reação mais refinadas no software.

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Predicting the Mechanical Performance of Cement-Based Materials from Quantum Chemical Calculations

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Keywords: Computational Quantum Chemistry, Semiempirical Methods, Hydrogen Bonds, Cement-Based Materials.

Introduction

The chemistry of cement-based systems is often considered complex by scientists of construction materials. This is mainly because their studies are generally carried out from macro and micro perspectives. The cement-based materials, such as the mortars, are usually prepared by mixtures of Portland cement, sand, hydrated lime, and water. In this sense, important performances of these materials include the mechanical properties. These properties are strongly affected by the water quantity employed in their processing. Therefore, we developed a simple strategy to predict the nature of strength of three mechanical properties (compressive, flexural, and adhesion strengths) from a computational quantum chemistry perspective. For this, the role of hydrogen bonds on the mechanical properties of a set of cement-based mortars was investigated by performing quantum chemical calculations.

Methodology

The AM1, PM3, PM6, and PM7 semiempirical methods were considered in order to fully optimize the geometry of the hydrogen-bonded complexes between the main inorganic compounds ($\text{Ca}(\text{OH})_2$ and SiO_2) of the cement-based mortars and a set of water clusters ($(\text{H}_2\text{O})_n$), being $n = 2-5$. The solvent effects of the water were also considered by employing the COSMO model. Thermodynamic properties were also calculated. All calculations were performed by employing the MOPAC 2016 software.

On the other hand, three types of cement-based mortars were prepared by using different proportions of Portland cement, hydrated lime, and sand: 1:2:9 (weak mortar); 1:1:6 (intermediate mortar); and 1:0.5:4.5 (strong mortar). Finally, after the cement-based materials have dried for 28 days, the mechanical properties of compressive, flexural, and adhesion strengths were measured. All details can be accessed in the article associated with this work¹.

Results and Discussion

By considering the AM1, PM3, PM6, and PM7 semiempirical methods, only the PM7 was capable to fully optimize the geometries of the hydrogen-bonded complexes. In this sense, the enthalpy of formation average of the hydrogen-bonded complexes is shown in Table 1, in which the complexes are predicted to be energetically favorable to be formed by considering both isolated and aqueous conditions.

Table 1. Average of the PM7 and PM7/COSMO values of the formation of the hydrogen-bonded complexes.

Complex	ΔH_f^{PM7} (kJ/mol)	$\Delta H_f^{\text{PM7/COSMO}}$ (kJ/mol)
$[\text{Ca}(\text{OH})_2] \cdots (\text{H}_2\text{O})_{2-5}$	-50.9	-29.7
$[\text{SiO}_2] \cdots (\text{H}_2\text{O})_{2-5}$	-43.9	-27.1

Because the cement-based mortars are prepared and applied in the paste form, we considered the $\Delta H_f^{\text{PM7/COSMO}}$ values and the mol quantities of both $\text{Ca}(\text{OH})_2$, X, and SiO_2 , Y, and it was possible to estimate the hydrogen bond strengths (ΔH_{HBS}) of these materials by the following equation:

$$\Delta H_{\text{HBS}} = \Delta H_f^{\text{PM7/COSMO}} [\text{Ca}(\text{OH})_2] \cdot (\text{H}_2\text{O})_n + \frac{Y}{X} \Delta H_f^{\text{PM7/COSMO}} [\text{SiO}_2] \cdot (\text{H}_2\text{O})_n$$

All ΔH_{HBS} values were calculated, and we verified that they are strongly correlated with the measured mechanical performances of the materials (Figure 1).

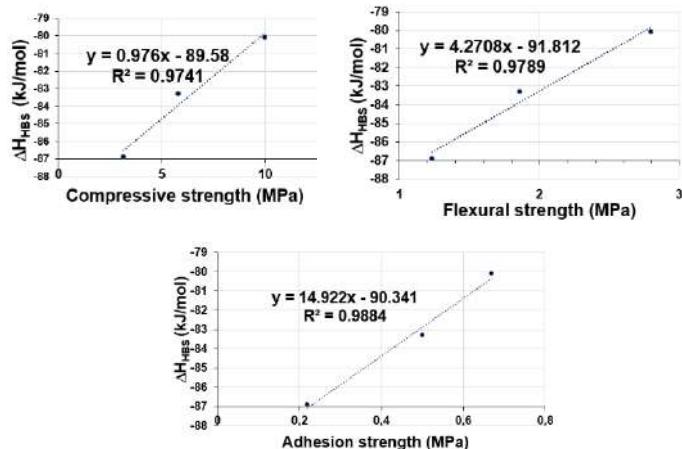


Figure 1. Linear regressions between the calculated ΔH_{HBS} values and the measured mechanical properties.

Conclusions

By calculating the ΔH_{HBS} values, the nature (weak, intermediate, or strong) of the mechanical performances of cement-based mortars can be predicted, and the quantum chemical calculations revealed that weak hydrogen bonds are associated with high mechanical performances.

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Modeling the Continuous Bright White Light Emissions by Energy Upconversion in Nanomaterials

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Key words: energy upconversion processes, white light, lanthanide ions.

Introduction

Light emissions by upconversion are processes in which lower energy photons are converted into higher energy photons. For example, excitation in the near infrared (NIR) region causes emissions in the visible region. These processes have several applications ranging from photovoltaics and lighting to nanomedicine, which are of great interest. In the last decade, a bright white light emission with a continuous spectrum was observed when exciting some materials, in particular, metal oxides, with high power density (laser) sources at the NIR region. The origin of this phenomenon is not yet established, which is the motivation for developing and implementing a quantitative model.

Methodology

This model was based on the power balance equation in which the energy absorbed from the excitation beam is dissipated by heat transfer (e.g., thermal conduction), by internal heating (thermal capacity) and by thermal emission of white light (blackbody type). The numerical solution of the differential equation obtained in the model was successfully implemented and provided results without the approximations used in the analytical solutions. The temporal dependence of temperature and of the continuous broad bright white light emission by energy upconversion in (nano)materials were obtained and compared with experimental observations and data.

Results and Discussion

All the main features of these continuous bright white light emissions were explained and quantified by the analytical and numerical results. In particular, the dependence of the integrated emission intensity on excitation source power (Figure 1), on the particle size and sample porosity and doping, on the ambient pressure and temperature, as well as the existence of a power density threshold of the excitation source and the non-exponential temporal decay of white light emission (Figure 2). It has also been shown the reasons for the white light emissions obtained by upconversion being so bright and intense, similar to incandescent bodies (Figure 3).

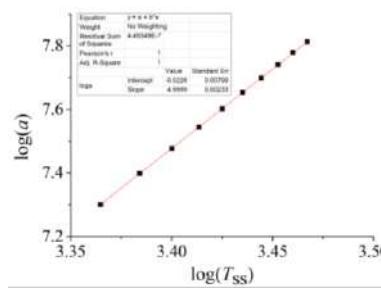


Figure 1. Dependence of steady state temperature with the excitation source power density.

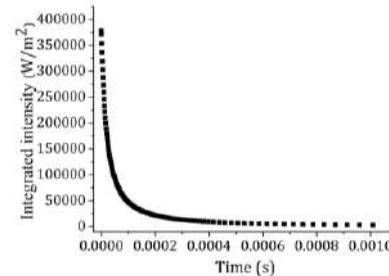


Figure 2. Time dependence of integrated emission intensity with the excitation source off.

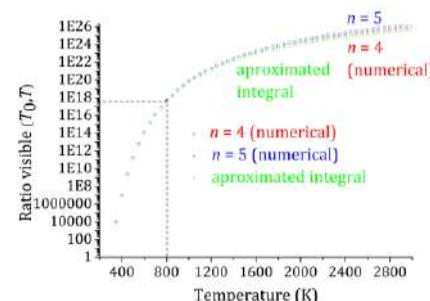


Figure 3. Ratio of the emissions in the visible region for temperatures ranging from 300 to 3000 K.

Conclusions

The results obtained and their comparisons with experimental data suggest that the proposed model has been validated and describes quantitatively all the features of this process, and can be used to design new, more efficient materials and improve experimental conditions.

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Beyond *de novo* design: chemical descriptors in the driving seat

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Keywords: DOCK6, *de novo* design, cheminformatics descriptors.

De novo design is a well-known strategy for exploring the chemical space in computational chemistry. Given an ensemble of molecular fragments, it is possible to virtually generate an infinite set of different molecules with uses spanning from lead discovery to materials science. However, *de novo* design's power can also be its most significant challenge: *de novo* design programs might generate a plethora of compounds disregarding any physical-chemical properties of interest. UCSF DOCK6 partially solves this issue by using scoring functions that restrict growth to the region of chemical space with the best scoring molecules. We recently extended the DOCK6 *de novo* design algorithm to include descriptor calculations throughout the stages of molecular growth to restrict even further the search in chemical space.

A DOCK6 conversion engine that allows the use of RDKit C++ API methods is a pivotal piece of the algorithm. As the fragments are connected and form partial or complete molecules, DOCK6 calculates the descriptors and accepts or rejects the candidates based on user-defined parameters. The methodology currently allows the selection of molecules with desirable values of logS, logP, number of stereocenters, drug-likeness, and synthetic accessibility. We call this methodology descriptor-driven *de novo* design (D3N). Instead of driving growth using a hard cutoff that discards all potential candidates with descriptors outside a pre-determined range, D3N allows the acceptance of some outliers using a soft cutoff scheme. The soft cutoff is necessary because it enables greater chemical diversity in the final results and makes sure that partially grown molecules with unsatisfactory descriptors have a chance of generating satisfactory molecules in later stages of growth. We validated the methodology using two types of calculations: a performance analysis of D3N simulations without proteins constraining ligand growth (DOCK6 simple_build) and the construction of new ligands in 57 known drug targets. Simulations were run using narrow descriptors' ranges (D3N-tight), broad descriptors' ranges (D3N-loose), and no descriptor limitations (D3N-no).

The analysis of the results was very encouraging. D3N-tight successfully generates a more significant fraction of molecules with descriptors within the user-defined range than D3N-loose and D3N-no without significantly increasing simulation time. We also

verified that D3N-loose and D3N-no generate virtually identical descriptor distributions if the user-defined descriptor range for D3N-loose is large enough. Additionally, it is possible to create molecules such that the descriptors distributions are as narrow or broad as the user needs. Finally, drug target analysis revealed that D3N-tight generates up to 6 times more unique molecules than simply running a regular *de novo* simulation and filtering the results.

Machine and Deep Learning Models to Predict Acetylcholinesterase Activity

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Keywords: Alzheimer Disease, Drug Design, Machine Learning, Docking, Deep Learning.

Introduction

Alzheimer's disease (AD), a neurodegenerative disease characterized by progressive loss of cognitive functions, is the most prevalent type of dementia worldwide, accounting for 60 to 70% of cases. AD pathogenesis seems to involve several factors, including deficiency in cholinergic transmission. The drugs available (galantamine, rivastigmine and donepezil) are for symptomatic treatment and have several adverse effects such as hepatotoxicity, hypertension, and weight loss. There is urgency in finding new drugs capable of preventing the progress of the disease, controlling symptoms, and increasing the survival of patients with AD. The goal of this study is built a Machine Learning model able to predict the activity of compounds against the main molecular target involved with AD, acetylcholinesterase [1].

Methodology and Results

Forty acetylcholinesterase inhibitors were obtained from ChEMBL; 40 false-positive compounds were obtained from DUD-E (<http://dude.docking.org/>). All compounds were refined by the run_mopac [2] using the Eigenvector Following (EF) routine and the parametric method 7 (PM7) of MOPAC. Following, the compounds were docked using Autodock Vina [3] into the binding site of acetylcholinesterase (PDB: 4M0E). The cLogP, number of hydrogen bonds donors group, polar surface area and Autodock Vina binding energy were used to generate the dataframe for Machine and Deep Learning models. The biological activity was the target to be predicted, which active and inactive compounds were signed as 1 and 0 values respectively. Thus, supervised models, K-Nearest Neighbors (KNN), Decision Tree, Multilayer Perceptron (MLP), Support Vector Machine (SVM) and Deep Learning, were generated through Jupyter Notebook. As a result, the MLP was highlighted among all models with the best accuracy of 0.84 (Figura 1).

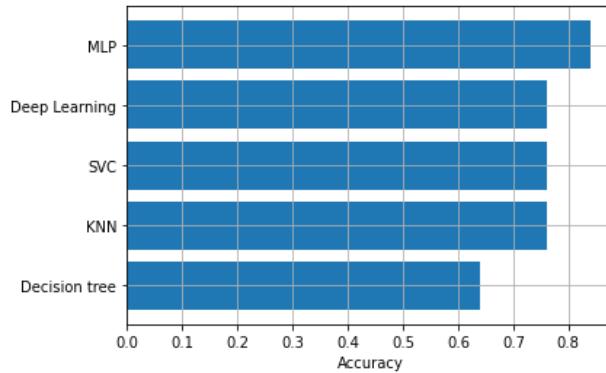


Figura 1. Machine and Deep Learning Models able to predict inhibitor activity against acetylcholinesterase.

Conclusions

Models were built using features of two different approaches, ligand and structure based drug design. In other words, our models were able to consider the pharmacokinetics and pharmacodynamic phases. The pharmacokinetics phase has a relevant role considering that the compounds have to cross the blood-brain barrier for example; whereas the pharmacodynamics is relevant for the interaction drug-receptor. Finally, the MLP model can contribute to the development of new compounds for the treatment of patients with Alzheimer's disease.

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Disulfiram derivatives as potential PLpro inhibitors: an *in silico* study

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Palavras-Chave: COVID-19, protease, molecular docking.

Introduction

The main protease (Mpro) and papain-like protease (PLpro) from SARS-CoV-2, which causes the COVID-19, are essential enzymes for viral replication (Francés-Monerris *et al.* 2020). Many efforts have been done in the search for SARS-CoV-2 proteases' inhibitors. Disulfiram (DSF) was found to inhibit PLpro ($IC_{50} = 6.9 \mu M$) interacting with Cys residues (Ma *et al.* 2020). In this sense, blocking the thiol moiety from the catalytic triad of PLpro (Cys111, His272, and Asp286) is a good strategy to inhibits this enzyme. Here we search for approved analogs drugs of DSF and simulate their binding pose in the active site of PLpro, by molecular docking, with the aim to verify their potential inhibitory activity.

Materials and Methods

With the attempt to find DSF analogs, a search was made on Drug Bank (web database), where the Thiram and dipentamethylenethiuram disulfide (DPTD) molecules were found as approved drugs. Density functional theory (DFT) calculations (B3LYP-D3(BJ)/6-311G(d,p)) (Madabeni *et al.* 2021) were done to optimize the molecules and to compute the condensed Fukui functions. Docking simulations were carried out according to the literature (Nogara *et al.* 2021), using the AutoDock Vina program (Trott and Olson 2010) and PLpro structure from the Protein Data Bank (PDB ID 7JN2).

Results

The predicted binding poses obtained from the docking studies focusing on the active site demonstrated that the sulfur atom from the disulfide bond of DSF is able to interact with the thiol moiety of Cys111 (4.5 Å). These data indicate that the thiocarbamoylation of the Cys111 could be possible, and could lead to the PLpro inhibition. In fact, the analysis of the Fukui function (f^+) indices of DSF and analogs suggest that the sulfur atoms are the most reactive site for the nucleophilic attack by the catalytic cysteine residue (Cys111) than the carbon of thiocarbonyl moiety. Thiram presented an S···C=S interaction with 4.9 Å and the DPTD showed an S···S interaction (5.4 Å) with the Cys111, suggesting a poor binding pose and activity than the DSF (Figure 1), despite the predicted binding free energies, ΔG (for DSF, Thiram, and DPTD = -2.9, -3.1, and -3.8 kcal/mol, respectively). The replacement of the ethyl moieties of DSF by methyl and piperidinyl groups from Thiram and DPTD, respectively, suggest

decreasing the PLpro covalent inhibition because it interferes in the molecule's binding pose.

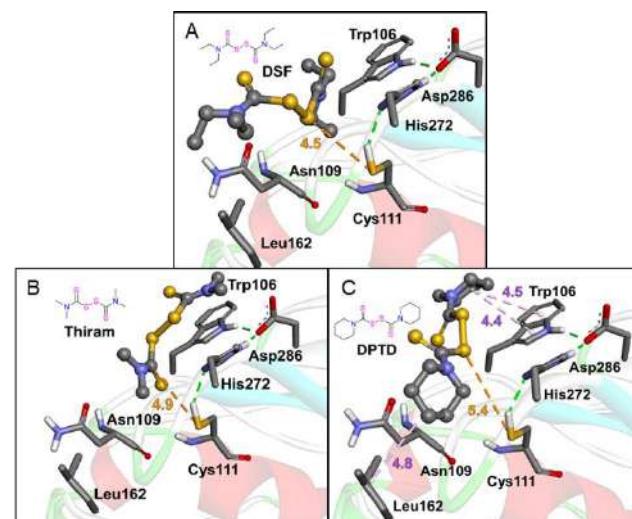


Figure 1. PLpro docking with DSF (A), Thiram (B), and DPTD (C).

Conclusion

The data presented here suggest that new molecules analogs to DSF, including Thiram and DPTD, could be tested in *in vitro* and *in vivo* trials to confirm the inhibitory and pharmacological potential. Thiram and DPTD appear to be less effective than DSF. The replacement of the ethyl groups of DSF could be an option to design new molecules with better PLpro affinity.

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Mecanismo de reação do 1-cloro-2,4-dinitrobenzeno com o radical hidroxila: um estudo de DFT

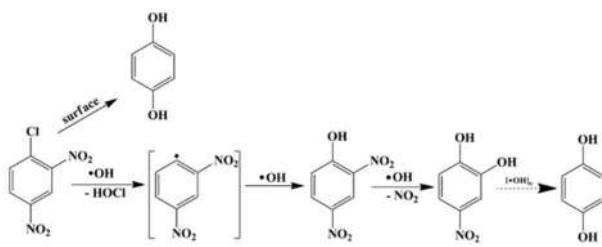
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Palavras-Chave: 1-cloro-2,4-dinitrobenzeno, radical hidroxila, DFT

Introdução

A molécula 1-cloro-2,4-dinitrobenzeno (DNCB) é um composto aromático que pertence à família dos organoclorados e grupos nitro que são muito tóxicos para organismos aquáticos e pode causar efeitos negativos de longo prazo em o meio ambiente, bem como é considerado um agente cancerígeno. Devido à complexidade da estrutura molecular do DNCB, que possui dois grupos nitro (-NO₂) e um grupo cloreto (-Cl) (Freire et al., 2000), sua eliminação da água é difícil porque a grupos nitro conferem uma alta estabilidade química à molécula e uma ótima resistência à degradação química e biológica (Xu et al., 2008; Liu et al., 2012). Tendo em vista a complexidade da degradação, tentaremos propor os caminhos de reação mais favoráveis utilizando métodos computacionais.



Fonte: Santos, 2020.

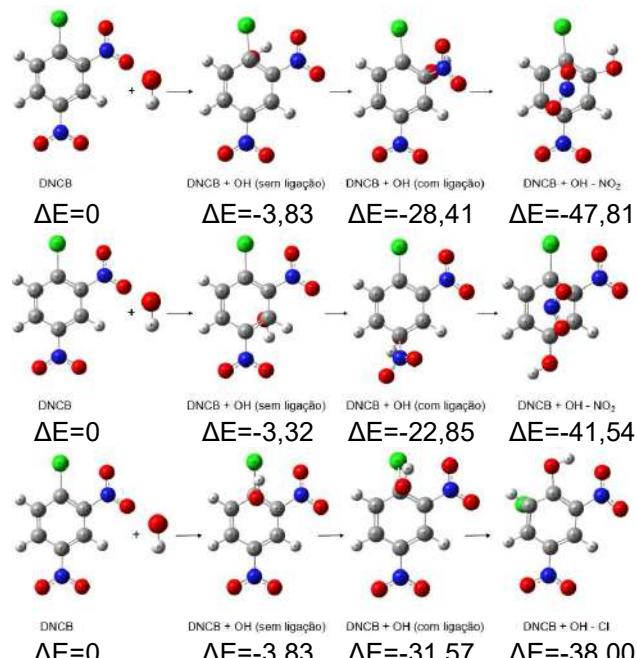
Metodologia

As geometrias dos compostos estudados foram otimizadas a partir dos níveis teóricos: B3LYP, M06-2X, PBE1PBE e BHandHLYP e a análise vibracional das geometrias otimizadas foi feita a fim de determinar se as geometrias resultantes apresentavam frequências imaginárias ou não. Os cálculos foram realizados utilizando o pacote Gaussian 09.

Resultados

Foram realizados cálculos para os possíveis ataques do •OH nas posições orto, meta e para ao anel aromático tanto em vácuo quanto em meio aquoso para alguns tipos de métodos de solvatação teóricos. Foi necessário calcular as Energias Gaussianas para os intermediários que foram encontrados. Todos os ΔE são calculados em relação à energia dos reagentes isolados: ΔE = E_{produto}-E_{OH}-E_{DNCB}.

M06-2X/6-31++G(d,p) em água (PCM)
ΔE(Kcal/mol)



Conclusões

Em todas reações do ataque do radical hidroxila ao DNB, foi possível observar que o ataque mais favorável é na posição orto ao cloro, como podemos observar no resultado obtido com o método M06-2X/6-31++G(d,p) em água utilizando o método de solvatação (PCM).

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Benzazóis como potenciais sondas fluorescentes de DNA: Docking e Dinâmica Molecular

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Palavras-Chave: ESIPT, benzazóis, Modelagem Molecular.

Introdução

O imageamento celular utiliza cada vez mais sondas fluorescentes. O principal problema dessas é que as estruturas bioquímicas também apresentam fluorescência, gerando resultados insatisfatórios. Uma alternativa para esse problema é o uso de moléculas que apresentem o fenômeno *Excited State Intramolecular Proton Transfer* (ESIPT), acarretando em compostos que tem um elevado deslocamento de Stokes, obtendo-se melhores relações sinal-ruído. Os benzoxazóis, benzimidazóis e benztiazóis avaliados nesse estudo possuem fluorescência por meio do ESIPT.

Objetivo

Realizar um estudo de *Docking* de diversos benzazóis avaliando a afinidade desses pelo DNA, baseado em suas energias livres médias, além do modo de interação dos ligantes na biomolécula. A partir disso, selecionara-se os melhores compostos para execução da Dinâmica Molecular, a fim de estudar o comportamento desses benzazóis em condições fisiológicas.

Metodologia

Docking: Foi realizado no software AutodockTools4.0, utilizando o Dodecâmero de Dickerson-Drew com um *gap* de intercalação. 120 moléculas foram avaliadas, obtendo-se 100 conformações por molécula. Para validação do método, como referência para as moléculas propostas, foram realizados Dockings do DAPI (-8,29 kcal.mol⁻¹ bolsão menor; -7,05 kcal.mol⁻¹ intercalação) e do Laranja de Acridina (-6,87 kcal.mol⁻¹ bolsão menor; -7,05 kcal.mol⁻¹ intercalação), sondas comerciais amplamente utilizadas.

Dinâmica Molecular: Foi realizada no pacote GROMACS, utilizando-se do campo de força AMBER. A conformação inicial obtida pelo *Docking* foi centrada em um cubo, em um meio com pH= 7. Após as etapas de minimização de energia, submeteu-se o sistema a uma simulação de 200 ns.

Resultados

Foram selecionados os 5 melhores compostos provenientes do estudo com *Docking* (onde observou-se nos diferentes *clusters* de conformações apenas a interação com o bolsão menor ou intercalação) para realização da Dinâmica Molecular. O composto 2-[2'-amino-5'-N-(fenil)-fenil]6-dimetilaminobenzoxazol apresentou energia

livre mais negativa que o DAPI e o Laranja de Acridina em ambos locais de interação: (-8,7 kcal.mol⁻¹ bolsão menor; -7,95 kcal.mol⁻¹ intercalação), demonstrando indícios de se comportar como intercalante, buscando interagir horizontalmente com o DNA. O 2-[2'-hidroxi-5'-N-(fenil)-fenil]-5-aminobenzimidazol também foi superior às sondas comerciais em ambas as interações: (-8,61 kcal.mol⁻¹ bolsão menor; -7,58 kcal.mol⁻¹ intercalação), demonstrando ser um ligante de bolsão menor, ao sair do *gap* de intercalação e interagir com o bolsão menor.

O 2-[2'-amino-4'-N-(fenil)-fenil]-6-aminobenzimidazol também mostrou-se superior às sondas comerciais na interação com o bolsão menor (único local de interação do composto: (-8,95 kcal.mol⁻¹). Os compostos 2(2'-amino-4'-dimetilaminofenil)-5-aminobenzimidazol (-8,16 kcal.mol⁻¹) e 2(2'-hidroxi-5'-aminofenil)-6-aminobenzimidazol (-7,7 kcal.mol⁻¹) foram superiores somente ao Laranja de Acridina no bolsão menor. As três últimas moléculas interagiram favoravelmente no mesmo sítio na Dinâmica Molecular, único *cluster* identificado no *Docking* para essas moléculas.

Conclusões e Perspectivas

Foi possível realizar uma triagem virtual (*docking* e dinâmica molecular) de 120 benzazóis, chegando a 5 compostos promissores, que demonstraram interagir com o DNA. Esses compostos terão sua energia livre calculada (usando o método MM/PBSA), e futuramente serão sintetizados, para avaliação fotoquímica e biológica.

Agradecimentos

Ao CNPq pelo financiamento e bolsas (bolsa produtividade S.C.G. processo 310282/2020-9; bolsa produtividade P.A.N. processo 305041/2017-7).

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Docking de candidatos a fármacos na albumina do soro bovino.

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Palavras-Chave: Docking, Drug Discovery, BSA.

Introdução:

Os métodos computacionais no desenho racional de fármacos permitem complementar resultados experimentais e propor possíveis fármacos. Um dos métodos utilizados é a docagem molecular, que estima a tendência de um ligante se ancorar em regiões de um receptor macromolecular¹. Uma aplicação importante é a interação entre um possível fármaco e uma proteína transportadora, como a albumina do soro bovino (BSA)² usada por ser homóloga à albumina do soro humano (HSA), com custo inferior. Ambas são proteínas fluorescentes, e a fluorescência da BSA é atribuída aos resíduos triptofano (TRP) TRP134 e TRP213. O objetivo desse projeto é através de docagem molecular ligante-proteína investigar interações das moléculas de interesse com regiões que contenham TRP da BSA, complementando estudos de fluorescência de laboratórios parceiros.

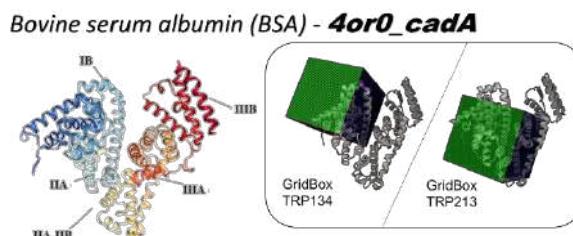


Figura 1. A esquerda a imagem da cadeia A da BSA com os subdomínios indicados e a direita de forma comparativa as respectivas GridBox utilizadas.

Metodologia:

As moléculas estudadas se dividem em 3 grupos: grupo N com 4 moléculas que variam entre a posição do naftil e com e sem metacrilato; grupo F que possui uma estrutura em comum com o N, porém alterna entre diferentes grupos retiradores, ambos com centro quiral, o terceiro grupo é o de 3 híbridos lofinacinamamida alterando o tamanho da cadeia. Após a construção e otimização das estruturas dos ligantes³, e de posse também da estrutura cristalográfica da BSA submete-se os sistemas aos cálculos de docagem nos programas AutoDock 4.0⁴ e Vina⁵. A análise é feita visualmente levando em conta a posição do ligante, o escore da interação (quanto mais negativo mais favorável) e as conformações.

Resultados:

Para os grupos N e F quiralidade não foi relevante e houve uma tendência de escores mais negativos na proximidade do TRP213 e de número maior de

conformações no TRP134. Para o grupo LOFINAS foi possível definir a preferência do ligante pela interação próxima do TRP213 tanto em energia e conformações.

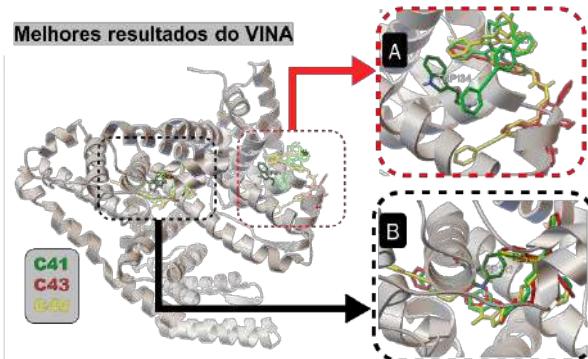


Figura 2. Os melhores resultados do grupo LOFINAS gerados pelo VINA, onde C41 a C45 aumentando a cadeia são representados em verde, vermelho e amarelo respectivamente, (A) TRP134 e (B) TRP213.

Considerações finais:

Os grupos N e F apresentam resultados promissores e ainda devem ser discutidos junto com os resultados experimentais. Já para o grupo LOFINAS, já discutido juntamente com os dados experimentais, concluiu-se que há a formação de um complexo mais estável na região e bem próximo do TRP213.

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Investigação da imobilização de As⁵⁺ em superfícies de óxidos e oxihidróxidos de Ferro e Alumínio

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Palavras-Chave: DFT, Imobilização de arsênio, óxidos e oxihidróxidos.

Introdução: Contaminação do solo e sistemas aquáticos por arsênio (As) é uma preocupação ambiental global.¹ A remediação da contaminação de solos é cada vez mais realizado com uma tecnologia emergente baseado na imobilização de As em óxidos e oxihidróxidos de ferro e alumínio.^{2,3} Goetita (α -FeOOH, **Goe**), hematita (α -Fe₂O₃, **Hem**) e seus isomórficos diáspero (α -AlOOH, **Dia**) e coríndon (α -Al₂O₃, **Cor**), constituem as principais ocorrências naturais para óxidos e oxihidróxidos de ferro e alumínio.⁴ No presente estudo, as geometrias de adsorção competitivas para arsenato nos conjuntos de superfícies {Goe, Dia}-(010) e {Hem, Cor}-(001), bem como as respectivas energias de adsorção desses complexos na superfície, foram estimadas usando Teoria do Funcional da Densidade com condições periódicas de contorno (DFT-PBC) e ondas planas conforme implementada no pacote de software Quantum ESPRESSO.⁵

Metodologia: Os conjuntos {Cor, Hem}-(001), {Dia, Goe}-(010) foram simulados usando modelos de *slab* construídos com a mesma configuração apresentada no trabalho de Guimarães et al.⁶ Os cálculos foram realizados com a primeira zona de Brillouin centrada no ponto- Γ e a energia de corte foi escolhida em 50 Ry (680 eV). A energia de adsorção ($\Delta E_{As(V)}^{ads}$) foi estimada utilizando a Eq. 1.

$$\Delta E_{As(V)}^{ads} = E^{Surf+As(V)} - E^{Surf} - E^{As(V)} \quad (1)$$

No qual $E^{Surf+As(V)}$ é a energia da superfície com a espécie de As(V), E^{Surf} é a energia da superfície e $E^{As(V)}$ é a energia da espécie de H₃AsO₄ isolada, calculada utilizando uma caixa com as mesmas dimensões do *slab* e o mesmo protocolo de cálculo. Investigamos a adsorção em três sítios de adsorção distintos, Figura 1.

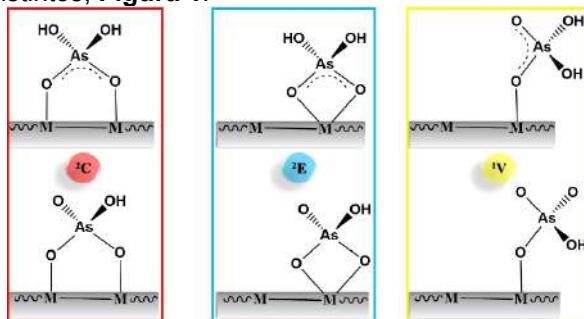


Figura 1 – Mecanismos avaliados para as superfícies – ²C; ²E; e ¹V.

Resultados: A Figura 2 sumariza $\Delta E_{As(V)}^{ads}$ para dois mecanismos de adsorção. No primeiro mecanismo, o H₂AsO₄⁻ se adsorve e um próton é transferido para um grupo oxo da superfície. No segundo mecanismo, o HAsO₄²⁻ se adsorve e dois prótons são transferidos para grupos oxo da superfície.

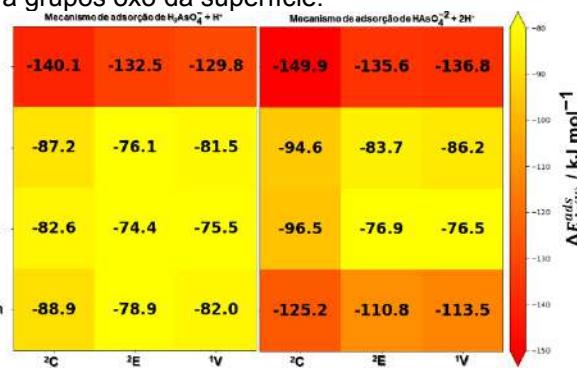


Figura 2 – $\Delta E_{As(V)}^{ads}$ em função do mecanismo e superfície.

Os resultados demonstram que espécies de As adsorvem na superfície dos óxidos e oxihidróxidos de ferro e alumínio no mecanismo ²C com distâncias médias As – Fe e As – Al da ordem de 3,28 e 3,23 Å, respectivamente.

Conclusões: O sítio de adsorção ²C é o mais favorável para todos os oxihidróxidos estudados. Os outros sítios de adsorção são pelo menos 8 kJ mol⁻¹ mais alto em energia. A estabilidade das espécies de As(V) adsorvidas nas diferentes superfícies investigadas aumenta na seguinte ordem: **Goe**-(010) < **Dia**-(010) < **Hem**-(001) < **Cor**-(001).

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Solvation effects on the p-Aminobenzoic Acid Protonation Dynamics by Ab Initio Molecular Dynamics

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Keywords: Proton transfer, ab initio molecular dynamics, microdroplets.

INTRODUCTION: Protonation equilibria are known to vary from bulk to microdroplet conditions, and is important, amongst others, in mass spectrometry field to define protonation sites of the formed ions in the gas phase. In the MS community, p-aminobenzoic acid (PABA) is a model system for probing the protonation dynamics in an evaporating droplet, and the final protonation site is highly dependent on the ionization parameters used, especially the solvent nature. While aprotic solvents maintain the solution protomer in the gas phase (N-protomer), when protic solvents are used, the carboxylic acid protonation in the gas phase (O-protomer) can be observed. In this work, we explore the protonation equilibrium of PABA solvated by different numbers of water molecules ($n = 0$ to 32) using ab initio molecular dynamics to explore how the proton transfer is impacted as the number of solvent molecules decreases, which mimics an evaporating droplet.

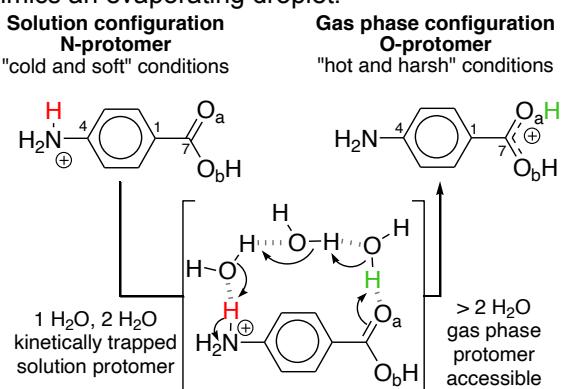


Figure 1. Representation of the protomers of PABA and a solvent bridge that would allow proton transfer and formation of the O-protomer in the gas-phase.

METHODS Protonated PABA was initially simulated with $n=32$ and $n=0$ water molecules, to obtain the solution and gas phase behaviors, respectively. From these results some geometrical parameters were selected that showed clear differences when either the O-protomer or N-protomer was present. Using the time evolution of those parameters, the PT events were analyzed for the clusters with varying number of water molecules.

The initial geometries of PABA were optimized using the plane wave (PW) module for the periodic boundary DFT code Quantum ESPRESSO (QE), version 6.0. Geometry optimizations and Car-Parrinello molecular dynamics (CPMD) simulations were performed with the PBE functional. Ultrasoft

pseudopotentials from pslibrary 1.0.0 were used to represent the effective nuclei. A kinetic energy cutoff of 130 Ry was used and Grimme's dispersion correction (D2) was included for all atoms. A fictitious electron mass of 400 au and a time step of 5.0 au (0.12 fs) were used. The simulation was carried out in the canonical ensemble (NVT) using a Nosé-Hoover thermostat with a target temperature of 350 K. The systems were equilibrated for about 3 ps following 220 ps of production run.

RESULTS AND DISCUSSION For $n = 8$ –32, the protonation is either at the NH_2 group or in the solvent network. The solvent network interacts with the carboxylic acid group, but there is no complete proton transfer to form the O-protomer as expected in the bulk. For smaller clusters, however, solvent-mediated proton transfers to the carboxylic acid were observed, mainly via the Grotthuss mechanism and very rarely the vehicle or shuttle mechanism (for $n = 1$). The kinetic trapping, previously reported as the rationale for the presence of solution-phase protomers in the gas phase, takes place in smaller clusters ($n < 6$ in the present system). Therefore, proton stabilization in the solvent network is shown to be the most relevant factor when explaining the origin of kinetic trapping. Solvent protonation is greatly stabilized in the larger clusters due to the hydrogen bond network, while the potential energy landscape controlling PT dynamics in smaller clusters is influenced by specific stable configurations. This observation is consistent with the fact that, at least from the experimental evidence available, solvents with higher proton affinity tend to yield kinetically trapped species, suggesting the kinetic trapping is essentially a gas-phase phenomenon. In that sense, the ability of the solvent network to retain proton may prevent PT between the protomers.

CONCLUSION The proton transfer dynamics in clusters of PABA with different number of water molecules showed that smaller clusters can lead to complete proton transfer from the amino to carboxylic group and shed light in the role of solvent molecules in the generation of different protomers during ionization.

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Molecule-surface potential energy function from adsorption second virial coefficient data using the non-linear Hopfield Neural Network

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Key-words: Non-linear Hopfield Neural Network, Virial coefficient, Energy potential function.

Introduction

The many-body problem in solid-liquid adsorption can be reduced in interactions atom-surface. This treatment is similar to the virial expansion for imperfect gases.[1]

At dilute solutions the terms higher than two can be omitted. Especially, the second virial coefficient has an important role on understanding the adsorption phenomena, since it depends directly of the potential energy between the adsorbate molecule and the adsorbent surface. In this work it is proposed a methodology to obtain the potential energy function for propionitrile-carbon surface from the thermodynamic property in an inverse framework.[2] Since the relation between the properties are not linear, the inversion procedure can be done using the non-linear Hopfield Neural Network (NLHNN). This approach is very stable, robust and was employed to solve several inverse problems in chemistry.[3]

Methodology

The NLHNN method consists in solving the following set of equations [3]

$$\frac{du_i}{dt} = - \sum_{j=1}^m (P_j^{calc} - P_j^{exp}) \frac{\partial P_j^{calc}}{\partial f_i}$$

in which f is called activation function and it is monotonically increasing with u , the neuron state. In this work, the term P_j^{calc} relates to the second Virial integral[4]

$$B(T) = \int (e^{-E_p(r)/k_B T} - 1) dr$$

with $E_p(r)$ the energy potential function, k_B the Boltzmann constant and T the temperature. The P_j^{exp} values are set as the experimental measurements for $B(T)$.

Results

The experimental data considered are presented in Table 1 along with results obtained by the NLHNN method and with those acquired by fitting the parameters ϵ and d in the modified Lenard-Jones 10-4 potential, given by

$$E_p(r) = \left[\frac{5(20)^{\frac{2}{3}}}{12} \right] \epsilon \left[\left(\frac{d}{r} \right)^{10} - \left(\frac{d}{r} \right)^4 \right]$$

This potential energy function was used since it is the result of averaging the Lennard-Jones 12-6 function over a surface.

The initial condition for solving the NLHNN set of equations was defined as the result presented in reference [4]. However, instead of using a model potential with parameters to be adjusted it was found the solution in a functional form, which enables a more accurate result.

Table 1 – Results for $B(T)$, in cm^3/g , obtained in reference [4] and in this work.

T / °C	0.1	25	70	R ²
B(T) _{exp}	983	478	101	-
B(T)[4]	914.34	404.60	126.59	0.9725
B(T)	995.76	436.70	134.90	0.9923

From the correlation analysis it is observed an improvement of the results acquired by the NLHNN with respect to those in reference [4].

Conclusions

The NLHNN method enables the acquisition of a potential energy function which retrieves the second virial coefficients more accurately than a parametric fitting. After this preliminary study, the code developed by the present authors will be improved and a study of the temperature range influence on the potential retrieved will be carried out. Moreover, this approach can be applied to retrieve the potential energy for several systems, since the behaviour of isotherms at low concentrations are linear.

Acknowledgements

This work was supported by CNPq – Brazil.

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Continuous Heterogeneous Model of Morphogenesis in Synthetic Chemical Cells

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Key words: Active droplets, far from equilibrium, spatiotemporal structures.

In a broad sense, morphogenesis is the generation of patterns and shapes, induced by the dynamical interplay between chemical and physical processes. [1] The earliest mathematical description of such an event was proposed by Alan M. Turing in his 1952 seminal article "The chemical basis of morphogenesis". [2] In this paper, Turing showed that the coupling between chemical reactions and diffusion could generate up to six spatiotemporal structures in a ring of identical biological cells. The British mathematician further speculated that one of these structures, a stationary pattern with a specific wavelength, could create asymmetries, leading to chemical and, consequently, physical differentiation. [3] Turing's model opened the door to a new view of developmental biology, however, it is still controversial in this context, because of the difficulties associated with the comparison between experiment and theory. [2,3,4,5]

Considering this last information, Tompkins et al. proposed in 2014 an abiological experimental setup for testing Turing's ideas. [3] Such experiment is carried out with synthetic "cells", i.e., aqueous droplets, stabilized by surfactants, in dispersed oil. Each droplet contains the Belousov-Zhabotinsky (BZ) oscillatory chemical reactants, which mechanism and dynamical behavior are well known. It is also known BZ reaction produces less polar intermediates, which can diffuse through the oil medium, creating channels of communication among cells. Technically, it represents an array of chemical oscillators coupled by diffusion. The authors reported the emergence of the seven spatiotemporal structures, six of them predicted by Turing and one not predicted, and astonishingly, they observed morphogenesis. [3]

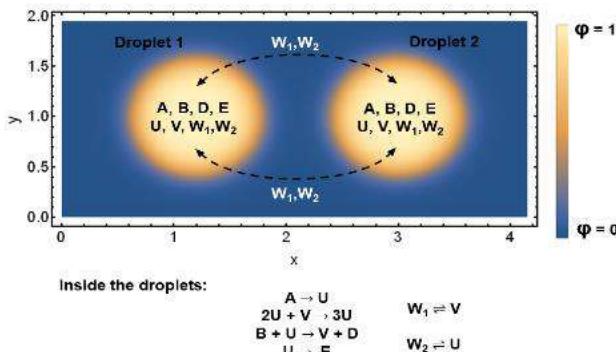


Figure 1: Schematic representation of the model proposed.

From that, we developed a continuous heterogeneous model for describing morphogenesis in synthetic chemical cells, see Figure 1. This model is based on the general theory of chemically active droplets that combines classical phase separation with reaction-diffusion systems. [6] From 2D calculations, we could observe the six spatiotemporal structures predicted by Turing and reported by Tompkins et al., in a linear array of droplets, and more importantly, under Turing instability, the chemical asymmetry triggers the physical differentiation, inducing morphological changes on the droplets, i.e., morphogenesis. Through this model, we are capable of understanding precisely the changes in chemical potential and osmotic pressure at each cell, provoked by the local difference in the consumption rate of chemical reactants, and correlating them to the physical transformations.

Little information from this system can be directly correlated to morphogenesis in biology, however, the experiment quantitatively explains this phenomenon in materials, which raises the possibility of application of such systems in material science. [3] Therefore, our model can be effective for elaboration/preparation of experiments and the understanding of events related to chemical/physical transformations.

Support: This work has been supported by the São Paulo Research Foundation (FAPESP) grants: 2019/23205-3 and 2019/12501-0 are kindly acknowledged.

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Rutin present in *Alibertia edulis* extracts acts on human platelet aggregation through inhibition of cyclooxygenase/thromboxane.^[1]

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Keywords: Molecular Dynamics simulation, Adaptive Biasing Force (ABF), COX-Rutin free-energy profiles.

Introduction

Platelets have played an important role in modulating inflammation, as a source of inflammatory mediators such as thromboxane, which is especially involved with pro-thrombotic processes and participation through adhesion molecules in the recruitment and modulation of leukocytes. Platelet response from the release of thromboxane A₂ (TXA₂) is mediated through Ca²⁺ dependent activation, cytosolic phospholipase A₂ kinase (cPLA2) and activation of cyclooxygenase type 1 (COX-1) that catalyzes free arachidonic acid (AA) favoring the synthesis of more prostanoids. In this sense, COX-1 inhibition is one of the main therapeutic tools in antiplatelet treatment. It is known that the main phenolic compounds found in the leaves of *A. edulis* are rutin, caffeic and vanillic acids. However, until now, no deeper study of the effects of *A. edulis* leaf extract (AELE) on platelet aggregation and its underlying mechanisms has been performed. In this vein, the present work evaluates the antiplatelet potential and the adjacent molecular mechanisms of the extract, as well as rutin, caffeic and vanillic acids present in the leaves, including a detailed molecular description of the COX-1 inhibition mechanism for rutin, which is an important protein for the AA conversion pathway (Fig. 1).



Fig. 1. Overall schematic description of the study.

Materials and Methods

All the chemicals were purchased from Sigma, Cayman Chemical, Cell Signaling and Santa Cruz Biotechnology. The *in vivo* assays were approved by Ethics Committee of Unicamp, protocols 99775118.5.0000.5404 and 5360-1/2019. The interactions of COX-1 with ligands at molecular level were evaluated according molecular docking, molecular dynamics simulations and adaptive biasing force method. The ABF method was applied to estimate the interaction energies via potential of mean force (PMF). Method details can be found in the original paper.^[1]

Results and Discussions

In this study, it is demonstrated that AELE, rutin and caffeic acid inhibit the platelet aggregation after stimulation of different agonists. They are characterized by the effects observed by AELE, rutin and caffeic acid on platelets via: (i) inhibition of platelet aggregation after stimulation of ADP, collagen, U-46619, AA and thrombin; (ii) decreased intra/extracellular calcium mobilization; (iii) decreased levels of thromboxane and phosphorylation of VASP157, VASP239 and PKC β_2 , at least in part by a COX-1 dependent pathway; and (iv) free-energy of protein-inhibitor (diclofenac, rutin and caffeic acid) dissociations, with further detailing of the mechanism of rutin stabilization at the COX-1 catalytic domain via specific residues, due to its similar profiles compared to diclofenac (Fig. 2).

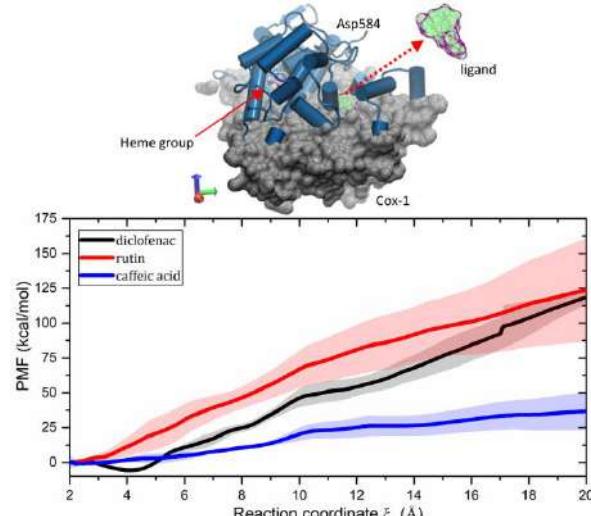


Fig. 2. PMF calculated by ABF method, in which estimates the COX-1-ligands energy of interactions.

Conclusions

The results provide evidence of the role of AELE, rutin and caffeic acid in platelet reactivity, allowing understand of its effects on the COX-1 pathway and the reduction of all signaling downstream. Also we suggest a mechanism for binding rutin and its main interactions to the catalytic site of COX-1.

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Enthalpy of formation of sodium and lithium compounds with EnAt1 and EnAt2

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Palavras-Chave: Lithium, sodium, composite methods

Introduction

Lithium and sodium are elements in group one of the periodic table, known as the alkali metals because they form alkaline solutions when they react with water. These atoms have just one valence electron. Magnesium is an element in group two of the periodic table. The elements in group two, which are all shiny and silvery-white in appearance, are known as the alkaline earth metals. Like the alkali metals, they form alkaline solutions when they react with water.

Computational Methods

The enthalpies of formation at 298.15 K were estimated from the total atomization energies. This needs an appropriate and balanced energetic account of the molecule and its constituent atoms, which places rigorous requirements on the quantum methods used. The results obtained atomization using the density functional theory (DFT) with different exchange and correlation: M06/aug-cc-pVTZ, BMK/aug-cc-pVTZ and composite methods: EnAt1 and EnAt2.

Results and Discussion

It is important to keep in mind that part of the excellent agreement with experiment for the composite methods tested in this paper arise from a cancellation of errors, as for example, those appearing from zero-point energy, geometry, truncation in the one- and n-particle basis sets, and neglect of core-core and core-valence correlation. Furthermore, the experimental values are generally accurate to just about 1 kcal mol⁻¹. To explain why some composite methods or some basis sets than others will require accurate benchmarking, where the error associated with every approximation is tested in detail.

The composite methods have spin-orbit correction and functionals DFT ones do not. For the chlorine and fluorine containing molecules, all of the atomization energies are extra-large. Insertion of the spin-orbit correction reduces the atomization energies of the chlorine and fluorine substituted molecules. In composite methods, it is known that incorporation of the spin-orbit correction results in better agreement between theory and experiment for the first-row fluorides, but not the second-row fluorides. We are aware there is little motive to question the security of the experimental data for the fluorine molecules.

Table 1: Comparison of EnAt1, EnAt2, BMK and M06. Methods for Calculation of ΔH_f (298 K) for 6 Molecules

	experiment - theory (kcal mol ⁻¹)				ΔH_f
	EnAt1	EnAt2	BMK	M06	Exp.
NaAlF ₄	-6.0	-5.6	-10.5	-5.1	-446.7
NaBr	-0.3	-0.4	2.1	0.4	-116
Na ₂ ⁻	1.0	3.7	0.0	-7.0	25
LiF	-0.3	-0.4	2.7	3.2	-80
Li ₂ F ₂	1.3	-0.3	-1.8	-1.7	-225.4
Li ₃ F ₃	1.3	-0.9	-2.4	-1.5	-362.6

Conclusion

In summary, it can be concluded that the accuracy of EnAt1 and EnAt2 for enthalpy formation is satisfactory when compared to DFT. In any case, EnAt1 and EnAt2 represent a successful step along a direction that can still be explored; from a more practical point of view, they are very robust and efficient in general. Heat formation was calculated for a set of widely used compounds of sodium and magnesium using a number of methods; EnAt1 and EnAt2 performed best against experimental values and are recommended for calculations

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Solvolytic mechanism of alkyl halides: the role of water as explicit solvent in S_N1 and S_N2 mechanism

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Keywords: Nucleophilic Substitution, Activation Strain Analysis, Explicit Solvation

INTRODUCTION

Organic reactions in aqueous media are becoming increasingly more frequent due to the necessity of using environmentally friendly solvents.¹ Besides, water can also act as reactant in solvolysis reactions. Solvolysis reactions have been reported for alkyl halides passing by a first-order nucleophilic substitution (S_N1), in a dissociative-associative mechanism ($D_N + A_N$).^{1,2} Concerted processes ($A_N D_N$), as second-order substitution (S_N2), also play a key role in these routes, as the reaction can pass by a borderline and/or merged mechanism (S_N1/S_N2)². According to these possibilities, we aim to understand the influence of explicit water molecules in S_N1 and S_N2 mechanisms in the solvolysis reaction of secondary alkyl halides (Figure 1).

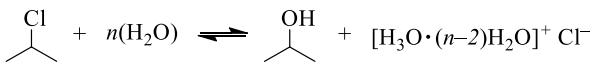


Figure 1: Solvolysis of 2-chloropropane.

METHODOLOGY

The number of water molecules ($n = 5, 9, 12$) was previously selected by Monte Carlos calculations. The $n = 3$ was also explored by adjusting two water molecules in the nucleophilic site and one stabilizing the leaving group. All calculations were made with M06-2X/aug-cc-pVDZ. A representative set of points obtained with IRC were analyzed by means of the activation-strain approach (along the C–Cl coordinate) to understand the interaction and distortion energies between the substrate (fragment 1) and the cluster of water (solvent, fragment 2). We also inspected the nature of the transition states using More O’Ferrall–Jencks plot of the bond orders calculated with NBO of C–Cl_{LG} (leaving group) and C–OH_{2nuc} (nucleophile).

RESULTS

Figure 2 shows the activation-strain analysis along the IRC. The highest energy barrier was calculated for $n = 3$ and 5 and the lowest one for $n = 9$ and 12. All transition structures are close to a carbocation (planar-triangle, 120°), suggesting a $D_N + A_N$ pathway (S_N1). However, IRC and frequency calculation point towards a concerted $A_N D_N$ pathway. The More O’Ferrall–Jencks plot (Figure 3) indicates that the TSs are highly loose, with a strong dissociative character, suggesting that the solvolysis pass by a highly loose S_N2 mechanism or by a merged one (S_N1/S_N2).

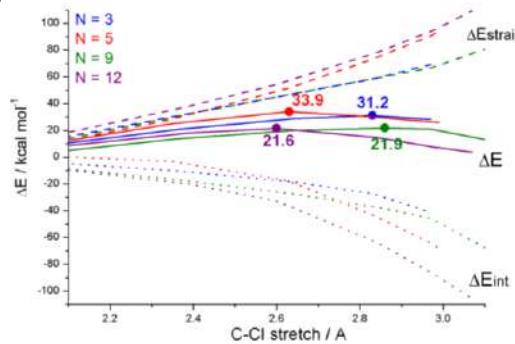


Figure 2: Activation strain analysis of reaction pathways with energies barriers identified.

According to the energy decomposition (Figure 2), interaction energy (ΔE_{int}) governs the barrier heights. Comparing the pathways with the earlier TSs ($n = 5$ and 12), the ΔE_{strain} is similar along the reaction pathway and the difference emerges from the interaction energy. The same behavior is observed for later TSs ($n = 3$ and 9). We attribute this to the leaving group stabilization. For $n = 5$ (highest energy barrier), there is only one water molecule interacting with the chloride anion. For $n = 3, 9$, and 12, there is a successive increase of water molecules (two, three and, four, respectively) around the chloride anion.

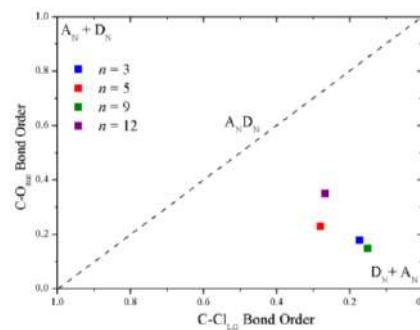


Figure 3: More O’Ferrall–Jencks plot for TS.

CONCLUSIONS

The increasing of water molecules solvating the TSs reduces the barrier height due to the interaction with the leaving group. In the following steps, we are going to perform the energy decomposition analysis (EDA) to gather more information regarding the driving forces that constitute the interaction energy and also to explore other secondary alkyl halides.

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Carbon nanohorn as nanocontainer for cisplatin: insights on the interaction with plasma membranes of normal and breast cancer cells

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Keywords: carbon nanohorns, cisplatin, plasma membranes.

INTRODUCTION

Cisplatin (cddp)-based chemotherapy is one of the most effective treatments for breast cancer, despite the severe side effects related to the high toxicity and low selectivity of this drug. In order to circumvent these drawbacks, the encapsulation of cddp into oxidized carbon nanohorns (CNHox) has been shown as a promising formulation with low toxicity, high biocompatibility and dispersibility in polar solvents due to their chemical functionalization with polar groups.^{1,2} These nanostructures include a tubular section (40-50nm) connected to a conical tip with a cone angle of 20°.³ In view of the literature gap referring to the biomedical application of CNH as drug delivery systems (DDS), a question that naturally arises is how this nanomaterial loaded with cddp molecules interacts with membranes of breast cells. In this sense, the present study involved modeling the 3cddp@CNHox complexes (three cddp molecules included in the CNHox) immersed in a physiological environment containing realistic plasma membrane models of normal and breast cancer cells and the analysis of the system by molecular dynamics (MD) simulations.

METHODS

Starting from a pristine CNH model,^{4,5} the oxidized model (CNHox) was built by following the oxidation mechanism with O₂ and H₂O previously described.^{5,6} Next, three cddp molecules were included in this CNHox, forming the 3cddp@CNHox complex (Fig.1).

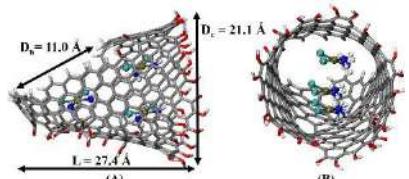


Fig.1 Initial structure of the 3cddp@CNHox complex. Side view (A) and the frontal view from the oxidized end (B).

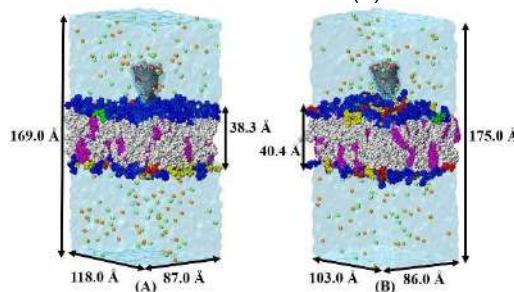


Fig.2. Initial structures of the two systems formed by the 3cddp@CNHox complex located near to plasma membranes of normal (A) and cancer breast (B) cells.

At last, two membrane prototypes were built based on experimental data referring to both composition and distribution of lipids found in normal (N_memb) and cancer (C_memb) cells of a typical human breast (Fig.2). The MD simulations ran at 310 K, 1.0 bar, and 0.15 M NaCl, during 800 ns of production, using the Amber16® software.

RESULTS

The van der Waals contribution played a primary role (74%) for the complex stability resulting in the trapping of the cddp cluster inside the CNHox. The results also revealed the interaction mechanism (Fig.3) of the 3cddp@CNHox with the biomembranes models, which is a multistep process including approach, landing, insertion, and penetration. The free energy calculations (MM/GBSA) indicated that the complex affinity by C_memb was 6.0 kcal mol⁻¹ more favorable than by N_memb due to a large number of hydrogen bonds.

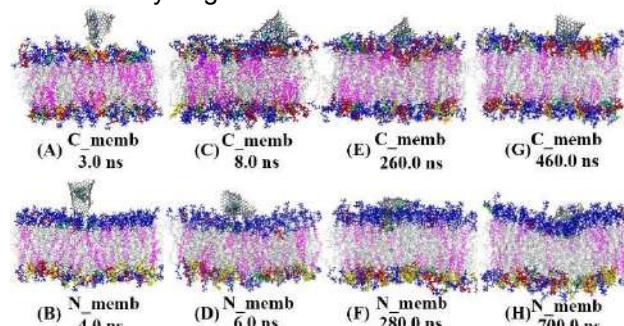


Fig.3 Interaction mechanism over 800 ns (simulation time) between the 3cddp@CNHox complex and the C_memb and N_memb membranes.

CONCLUSIONS

This study led to two conclusions suggesting the potential and selectivity anticancer function of the CNHox-based DDS for cddp: (i) the interaction of the DDS with cancer cells would be faster and stronger than with healthy cells, and (ii) once in the presence of cancer cell, the cddp releasing would be more favorable compared to normal cells.

Support: CNPq, FAPEMIG, CAPES

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TEORIA DA RESSONÂNCIA PARA A SUPERCONDUTIVIDADE METÁLICA

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Palavras-Chave: BCS, RVB, Supercondutores.

INTRODUÇÃO

Na teoria BCS [1], a temperatura crítica (T_c) tem ρ como a variável principal, sendo o produto do acoplamento elétron-fônons (V) com a densidade eletrônica no nível de Fermi (N_0):

$$T_c = \alpha e^{-\frac{1}{\rho}} \quad (1)$$

onde α é o produto da frequência de fônons pela temperatura de Debye do material. No cálculo de ρ , a transferência de elétrons na rede cristalina é descrita como uma ressonância das ligações químicas com a consequente variação dos raios e das valências dos átomos. A passagem do par de Cooper é associada a essa ressonância. Assim é possível classificar os supercondutores de calha pelo o aumento do raio do ânion em relação ao neutro, e os de crista pela diminuição do raio do ânion em relação ao neutro.

METODOLOGIA

A teoria da ressonância da ligação de valência (RVB) calcula a T_c usando como variáveis a carga atômica (z_i), o percentual de íons no cristal (p_i), valência média (v_{av}) e variação do raio atômico (ΔR)[2]:

$$T_c = 120e^{-\frac{1}{0,36v_{av}^3 \sum z_i p_i \Delta R}} \quad (2)$$

O cálculo das valências médias para 29 supercondutores e 5 não-supercondutores metálicos (todos, exceto os de terras raras) foi aqui realizado a partir das configurações eletrônicas resultantes da ocupação dos orbitais naturais gerados por cálculos HF/LanL1MB. Foi utilizado um modelo de cluster usando dados cristalográficos, com as valências das bordas saturadas com hidrogênio. A equação 2 permite, além do cálculo da T_c , classificar os metais em supercondutores de crista ($\rho > 0$) e supercondutores de calha ($\rho < 0$).

RESULTADOS

O procedimento utilizado separou corretamente os metais supercondutores dos não-supercondutores. Foram classificados 8 novos supercondutores de crista e 14 supercondutores de calha. O maior número de supercondutores de calha pode ser devido ao comportamento geral de sistemas atômicos, onde o raio atômico aumenta com a formação do ânion. Nos de crista, o raio atômico diminui.

A figura 1 compara a temperatura crítica calculada com a experimental.

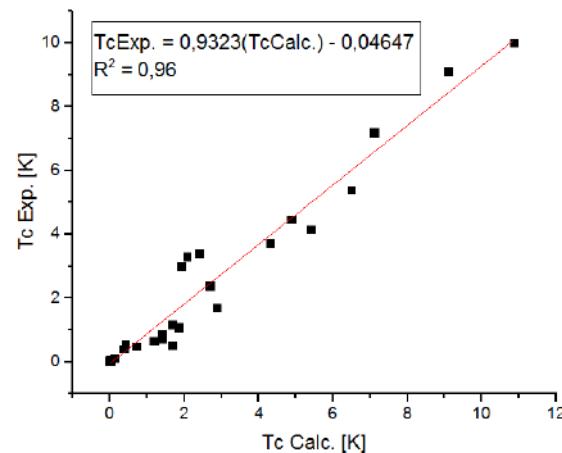


Figura 1 - Ajuste linear das Temperaturas críticas experimentais e teóricas dos metais

Os resultados estão em ótima concordância com os dados experimentais e com as previsões de Pauling para os supercondutores Y, Zr, Nb, Mo, Tc, Rh e Ru. Para o Mo, obtivemos $T_c = 1,40\text{K}$, a T_c experimental é $0,72\text{K}$ e a obtida por Pauling $2,92\text{K}$. Para os não-supercondutores foram observados valores menores de ρ em relação a qualquer um dos valores obtidos para os supercondutores. Nestes casos, o raio do ânion é menor do que o do neutro, um comportamento não convencional para sistemas atômicos.

CONCLUSÃO

As temperaturas críticas dos metais supercondutores foram calculadas utilizando a teoria RVB combinada com a Teoria de Orbitais Moleculares. Os resultados obtidos estão em ótima concordância com os dados experimentais. O procedimento separou devidamente os metais supercondutores dos não-supercondutores e ainda ampliou a classificação de supercondutores de crista e de calha.

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Modelagem MIA-QSAR das atividades anti-influenza de 2-iminobenzimidazolininas

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Palavras-Chave: MIA-QSAR, antivirais, 2-iminobenzimidazolininas.

Introdução

A influenza é causada pelo vírus da gripe, e seus sintomas podem ser leves ou graves. Essa doença se espalha mundialmente por surtos anuais, resultando de três a cinco milhões de casos de doença grave e cerca de 290.000 a 650.000 mortes.¹ A inibição da neuraminidase viral é um dos mecanismos de ação de drogas atualmente utilizadas para o tratamento da influenza. No entanto, o desenvolvimento de novos candidatos a fármacos deve ser constante, em razão do aparecimento de cepas resistentes. Uma ferramenta computacional muito utilizada no desenvolvimento e otimização de fármacos é a técnica QSAR (*Quantitative Structure-Activity Relationships*). Um método QSAR usando descritores moleculares baseados em análise multivariada de imagens (MIA-QSAR)² de estruturas químicas 2D foi aplicado para modelar os dados biológicos de 22 derivados de 2-iminobenzimidazolininas.³ O objetivo do presente trabalho consiste em comparar os resultados obtidos de uma análise MIA-QSAR tradicional com os resultados obtidos de uma análise aug-MIA-QSAR já publicado na literatura.⁴

Metodologia

Um conjunto de dados composto por 22 compostos derivados 2-iminobenzimidazolininas³ foi utilizado para construir dois modelos MIA-QSAR relacionando características estruturais com a bioatividade (pIC_{50}) e toxicidade (pCC_{50}). Inicialmente, foram geradas imagens bidimensionais (2D) dos compostos no programa ChemSketch (Figura 1) e, em seguida, tais representações moleculares foram sobrepostas e desdobradas em uma matriz binária de pixels, onde cada linha correspondia a uma molécula e as colunas aos valores de pixel para cada unidade digital das imagens. Com o auxílio da ferramenta Chemoface, foi gerado um modelo QSAR, utilizando-se o método de regressão por mínimos quadrados parciais (PLS). Os dois modelos gerados foram validados internamente (validação cruzada do tipo *leave-one-out* e *y-randomization*) e externamente (bootstrapping de 15 ciclos com 5 compostos de conjunto de teste escolhidos aleatoriamente).

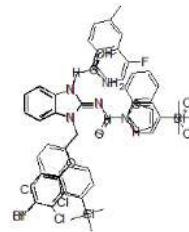


Figura 1. Imagens MIA sobrepostas.

Resultados

Os modelos para pCC_{50} e pIC_{50} com 4 variáveis latentes apresentou os seguintes resultados de pScore (%), correspondente à média percentual dos valores de r^2 de calibração e validações: 63.0 e 67.9. Ainda, os valores de pScore (%) na análise bootstrapping demonstram que os modelos são estáveis e robustos: pCC_{50} : 54.9 e pIC_{50} : 60.3, e que apresenta poder de predição tão bom quanto o obtido na abordagem aug-MIA-QSAR. Apesar de menos interpretável do que o aug-MIA-QSAR, o modelo tradicional MIA-QSAR baseado em wireframes de moléculas pode ser usado para a previsão das atividades antivirais de novos candidatos a fármacos, uma vez que demonstrou um melhor desempenho de previsão ($r^2_{\text{pred}} = 0.765$ e 0.714).³

Conclusões

Comparando a abordagem MIA-QSAR tradicional com a abordagem aug-MIA-QSAR⁴, observa-se que o poder de predição para abordagem tradicional apresenta um melhor desempenho, no entanto falha na interpretabilidade. Esta dicotomia aparente entre previsibilidade e interpretabilidade é de fato comum e complementar nos estudos QSAR.

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Modeling luminescence properties and their dependence on temperature in Eu³⁺-containing complexes

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Keywords: *intensity parameters, temperature, structural changes.*

Introduction

Complexes and materials containing lanthanide ions are widely employed in academic and technological researches, especially due to the unique features of the $4f-4f$ intensities transitions, which can be described by the (Judd-Ofelt) intensity parameters, Ω_λ , with $\lambda = 2, 4, 6$. These parameters are then used to comprehend their luminescent properties (e.g., lifetime, quantum yield). Another relevant aspect is the dependence of their photophysical properties with temperature, particularly, the dependence of luminescence lifetime and intensity parameters. It is formally known that the intensity parameters are temperature independent, except when considering the vibronic interactions¹. However, it has been observed that the transition intensities as well as the spontaneous emission rates, particularly of Eu³⁺-based systems, are temperature dependent. To explain these observations, it was proposed¹ that geometry deformations due to thermal effects cause variations on Ω_λ . In this context, this work aims at obtaining theoretical values of Ω_λ and emission lifetime at different temperatures for two complexes: (1) [Eu(hfa)₃bpyO₂]³⁺ and (2) [Eu(bpyO₂)₄]³⁺, which have known structures² and well-established photophysical properties.

Methodology

The calculations were performed following the usual procedures of optimization geometry, frequencies and electronic energies of ground and excited states using Gaussian09 program at DFT levels with basis sets and ECPs MWB52 for Eu³⁺, 6-31+G for O, N, and F, 6-31G for H and C; and semiempirical AM1/Sparkle level with MOPAC program. Five different structural changes were selected along several normal modes localized in the coordination polyhedron, denoted as: -1, -0.6, 0, +0.6 and +1, where 0 is the equilibrium structure. For each structure, it was calculated the energy transfer rates of selected levels, intensity parameters Ω_λ ($\lambda = 2, 4, 6$), quantum yield and lifetime using JOYSpectra software³ and their results were compared with experimental data².

Results

The calculated value of quantum yield was 38% for the (0) structure, which is in a good agreement with

the experimental² value of 40%. Theoretical lifetime was 0.71 ms, and the experimental² was measured as 0.70 ms. The experimental data of the intensity parameters (in 10^{-20} cm²) were $\Omega_2 = 33$ and $\Omega_4 = 9.33$, and these values can be compared to the theoretical ones depicted in Table 1.

Table 1: Theoretical values of Ω_λ (in 10^{-20} cm 2), quantum yield (Q) and lifetime (τ) for the (0) structure.

	Ω_2	Ω_4	Ω_6	$Q(\%)$	$\tau(\text{ms})$
-1	33.0	11.1	3.9	46	0.68
-0.6	33.0	10.3	2.7	56	0.71
0	33.0	9.7	2.0	38	0.71
+0.6	33.0	10.0	2.3	58	0.71
+1	33.0	11.5	3.7	34	0.70

Figure 1 shows an example of a simplified energy diagram for the non-deformed (0) structure, originated by JOYSpectra³, which shows the values of rates for different initial to different final states.

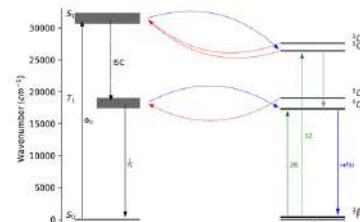


Figure 1: Energy level diagram

It was observed that the structural changes modified the energy values of the triplet states. The values of dipole-dipole, dipole-multipole, and exchange rates for the singlet states were also modified by the structural changes of the coordination polyhedron. These results can explain the thermal effects on the intensity parameters Ω_λ and transfer rates by the simulations on the coordination polyhedron.

Conclusions

We have obtained the thermal behavior for Ω_λ and different values for τ and Q based on structural changes in the coordination polyhedron, providing reasonable results and further analyses will consider the effects of different vibrational modes on the average values of properties and thermal effects.

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Estudo teórico da fotofísica do composto fotossensibilizador 4,5-dibromorodamina metil éster (TH9402) utilizado em terapia fotodinâmica

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Palavras-Chave: Terapia fotodinâmica, TH9402, TD-DFT.

Introdução

A terapia fotodinâmica (TFD) é uma técnica voltada ao tratamento de câncer que promove reações fotoquímicas pela interação entre radiação, agente fotossensibilizador (PS) e oxigênio molecular. É uma forma de tratamento alternativa aos tratamentos convencionais. Os estudos a respeito das características fotofísicas, baixa toxicidade e estabilidade do composto 4,5-dibromorodamina metil éster (TH9402) corroboraram para que este seja caracterizado como um bom fotossensibilizador para ser utilizado em TFD. O composto pode ser empregado em tratamentos com transplantes autólogos de células tronco e se mostrou eficiente no tratamento de tumores sólidos. O conhecimento de metodologias eficientes, voltadas à realização de estudos fotofísicos de compostos, contribuí para o processo de desenvolvimento de PS inéditos.

Metodologia

A fotofísica do TH9402 foi investigada, calculando-se a constante de fluorescência e a taxa de cruzamento entre sistemas (K_{isc}), utilizando-se a regra de ouro de Fermi em conjunto com a teoria de Marcus. As constantes mencionadas também foram calculadas empregando-se o formalismo de integral de caminho, implementado no programa ORCA 4.2.1. Os efeitos da interação do fotossensibilizador com o DNA nas propriedades espectroscópicas do TH9402 foram avaliados. Foi realizado docking molecular entre as moléculas do PS e do octanucleotídeo d(AGACGTCT)₂, utilizando-se o programa GOLD 5.8.1. Calcularam-se os espectros dos complexos de TH9402@DNA no programa ORCA 4.2.1. Os resultados foram obtidos no laboratório eCsMo^{lab}.

Resultados

O cálculo realizado utilizando-se a regra de ouro de Fermi em conjunto com a teoria de Marcus resultou no valor de constante de fluorescência igual a $4,18 \times 10^7 \text{ s}^{-1}$ ^[1]. Quando empregado o formalismo de integral de caminho, o resultado obtido foi $5,40 \times 10^7 \text{ s}^{-1}$ ^[1]. O tempo de fluorescência calculado foi $2,2 \text{ ns}$ ^[1], valor que apresenta boa concordância com o experimental, $1,6 \text{ ns}$ ^[2]. Utilizando-se o formalismo de integral de caminho calculou-se um valor de constante de cruzamento entre sistemas ($10,1 \times 10^7 \text{ s}^{-1}$)^[1] mais próximo ao valor experimental ($16 \times 10^7 \text{ s}^{-1}$)^[2] do que empregando-se a regra de ouro de Fermi em combinação com a teoria de Marcus ($27,5 \times 10^7 \text{ s}^{-1}$)^[1]. A partir da análise dos resultados, espera-se que a desexcitação do composto envolva o cruzamento

dos estados S₁ e T₂. Observou-se também, que a constante de cruzamento entre sistemas envolvendo o estado S₂ é considerável ($0,89 \times 10^9 \text{ s}^{-1}$)^[1]. Uma vez, portanto, que o estado S₂ seja ocupado, espera-se o cruzamento S₂→T₃. O resultado do cálculo de docking molecular mostrou três configurações possíveis de intercalação do TH9402 no DNA. Cálculos de espectro de absorção foram realizados com as geometrias mais estáveis de cada uma das configurações obtidas e também com uma configuração tendo o PS atuando como groove binder. A interação do TH9402 com o DNA, em todas as conformações estudadas, resultou em deslocamento batocrômico e diminuição da intensidade da banda de absorção máxima do composto. Observou-se deslocamento batocrômico próximo de 90 nm em um dos casos e diminuição da intensidade de até 72%, quando comparados os espectros dos complexos TH9402@DNA com o espectro do PS isolado.

Conclusão

O cálculo da constante de fluorescência empregando-se a regra de ouro de Fermi em conjunto com a teoria de Marcus resultou em um valor de constante próximo ao valor obtido quando foi empregado o formalismo de integral de caminho. Ambas as abordagens resultaram no valor de tempo de fluorescência de $2,2 \text{ ns}$ ^[1], com boa concordância com o valor experimental $1,6 \text{ ns}$ ^[2]. Em relação ao cálculo da constante de cruzamento entre sistemas, o formalismo de integral de caminho foi o que melhor descreveu o resultado experimental, a partir do resultado espera-se que, uma vez no estado excitado, a desexcitação do composto envolva o cruzamento entre sistemas dos estados S₁ e T₂. A comparação dos espectros de absorção dos complexos TH9402@DNA com o espectro de absorção do PS isolado, mostrou o deslocamento batocrômico e a diminuição da intensidade da banda referente à transição principal no espectro. Essas observações indicam a interação do PS com o DNA, entretanto não podem ser utilizadas para especificar qual o tipo de interação ocorrida.

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Agradecimentos

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Estudo Computacional do Grau de Heterogeneidade de uma Superfície no Perfil de Isotermas de Adsorção do Tipo Langmuir-Freundlich

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Palavras-Chave: Adsorção, Simulação, Heterogeneidade da superfícies.

Introdução

O método de Monte Carlo (MMC) tem sido aplicado com sucesso em diversas áreas científicas, onde podemos destacar a Físico-Química Computacional. Nesse trabalho, o MMC foi aplicado na simulação da adsorção de moléculas em sítios ativos de uma superfície quadrada, contendo LxL sítios. A equação abaixo descreve o processo.



onde, A representa uma espécie em meio fluido, A_{ads} representa uma espécie adsorvida no sítio ativo (S). No equilíbrio, o sistema é descrito por meio da isotermia de Langmuir-Freundlich (ILF). Em contrapartida da isotermia de Langmuir (IL), na ILF introduz-se um expoente ($0 \leq \alpha \leq 1$), conhecido como índice de heterogeneidade. Se $\alpha = 1$, a superfície é homogênea e a ILF se reduz à IL. Quanto menor o valor de α , maior o grau de heterogeneidade da superfície¹. Nesse contexto, o objetivo desse trabalho é estudar o efeito da heterogeneidade da superfície no perfil das isotermas de adsorção simuladas computacionalmente usando o MMC.

Metodologia

A simulação considera uma superfície contendo LxL sítios ativos, na qual uma espécie pode adsorver e dessorver dinamicamente. O algoritmo proposto segue os seguintes passos: (a) sítio vazio selecionado; (i) uma espécie A colide no sítio com probabilidade p_A^α , se a colisão for bem-sucedida; (ii) a espécie adsorve com probabilidade $p_{ads}=1$. Senão, nada acontece e um novo sítio é selecionado; (b) sítio ocupado. (i) a espécie dessorve com probabilidade p_{des}^α , onde $p_{des}=\exp(-1/\gamma)$. Definimos $\gamma=k_B T/E_{des}$, sendo E_{des} , a energia média de dessorção dos sítios, k_B a constante de Boltzmann e T a temperatura do sistema. Senão, nada acontece e o passo (a) é executado. Quando os passos (a) e (b) são realizados L^2 , temos definido o passo de Monte Carlo (pmc). Calculam-se médias sobre o número de amostragem (N_s) e tempo de média (t_m) (no equilíbrio), após o tempo de relaxação (t_r). Os parâmetros foram: $L=50$, $N_s=10$; $t_m=200$ pmc; $t_r=400$ pmc; e $\gamma=1$. Nesse trabalho, p_A , p_{ads} e p_{des} estão relacionadas, respectivamente à fração molar (X), e às constantes de adsorção e de dessorção.

Resultados

A Figura 1 mostra o perfil de cobrimento da superfície, em função da fração molar da espécie em sistemas contendo distintos valores de α . As linhas sólidas foram calculadas teoricamente, por meio da ILF. Observou-se que a fração de cobrimento (θ) cresce com o aumento da fração molar (X) da espécie e que as curvas para distintos valores de α se interceptam quando a fração de cobrimento e a fração molar do componente alcançam, 50% e 36%, respectivamente. O comportamento observado relaciona-se com a expressão: $X=1/K$, onde K é a constante de equilíbrio de adsorção-dessorção ($K=p_{ads}/p_{des}$). Nesse contexto, o valor da constante pode ser estimado graficamente analisando-se o eixo das abscissas em $\theta=0,50$. Nessa figura, os valores estimados, para $\alpha=0,50$, foi $X \sim 0,36$ e $K \sim 2,77$, sendo esse independente da heterogeneidade. Além disso, para $X < 0,36$, o grau de cobertura foi maior para superfícies com maior grau de heterogeneidade e para $X > 0,36$, observou-se um comportamento inverso.

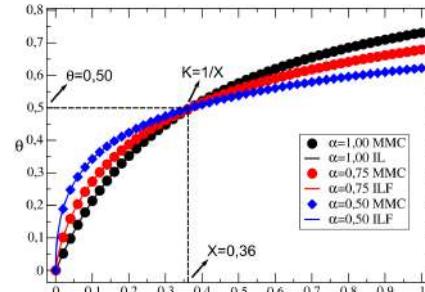


Figura 1.
Efeito da heterogeneidade da superfície.

Conclusões

O modelo proposto reproduziu satisfatoriamente as IL e ILF, elucidando o efeito da heterogeneidade da superfície nas isotermas simuladas. Observou-se que há uma relação entre o grau de cobertura e as constantes de equilíbrio de adsorção-dessorção para um dado valor de X, sendo independente de α .

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Quantification of molecular orbitals based on projection operators: applications to basicity prediction of organic compounds

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Palavras-Chave: Molecular orbital, HOMO-LUMO, FERMO, Acid-base behaviour, Localization degree, Γ_{FERMO}

One of the most critical applications of MOs in chemical phenomena is related to orbital HOMO and the orbital LUMO, whose energy difference is employed in the interpretation of the chemical reactivity^[1,2]. In face of some limitations^[2], another approach arose to understand the chemical reactivity: the FERMO (Frontier Effective for Reaction Molecular Orbital) concept^[3,4].

Our strategy to quantify the FERMO localization was based on the use of projection operators^[5]. We defined the degree of localization Γ_{FERMO} (Eq. 1) of a molecular orbital Θ_μ as the norm of a projected MO onto the expected set of atomic orbitals that are relevant to the reaction center of a given compound:

$$\Gamma_{\text{FERMO}} = \sqrt{\sum_l \sum_{i \in G} \sum_{j \in G} \sum_k C_{l\mu} S_{li} S_{ij}^{-1} S_{jk} C_{k\mu}} \quad (1)$$

The work was devoted to investigate which MO was the best for describing the acidity of amines, carboxylic acids, alcohols and phosphines, correlating PA with HOMO and FERMO energy, as seen in Figure 1.

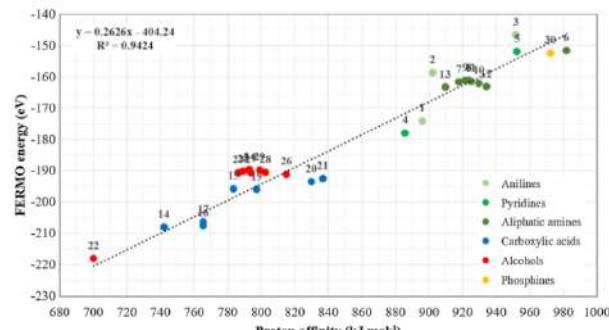


Fig 1: Correlation between PA values and FERMO energies for all the studied compounds.

This new method was employed for the analysis of the protonation reaction of 30 organic compounds. All structures were fully optimized in the gas phase with the software GAMESS. The DFT functional B3LYP and the basis set 6-31G(d,p) were employed.

It is known that, although the HOMO energies for families of compounds can be correlated with their PA values, there are many

cases for which this correlation is not good, requiring other parameters for linear regression analysis^[6]. Using the FERMO energies instead of those for HOMOs, a correlation with a R^2 value equal to 0.94 was obtained, indicating a tendency to increase the energy of the FERMO with the increase of the PA and, consequently, the basicity of the amines, carboxylic acids, alcohols and phosphines in the gas phase.

Our findings point out that the developed method allows us to obtain, with the application of the algorithm, different values of the localization degrees of MOs according to any combination of AOs. The FERMO concept can be applied to describe the acid-base behavior for different organic compounds, as demonstrated by the values of the coefficients provided by the new algorithm.

Acknowledgments

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Estudo computacional do espectro UV-Vis do calcitriol, principal forma biologicamente ativa da vitamina D

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Palavras-chave: *calcitriol*, UV-Vis, wB97XD/6-311++G(2df,p).

Introdução

A vitamina D auxilia na absorção de Ca²⁺ no intestino, resultando na manutenção dos níveis desse elemento necessários aos ossos.^[1] Ela possui ação protetora nos rins, coração e sistema imunológico.^[2] Vem sendo estudada como coadjuvante em tratamentos clínicos de câncer,^[3] porém, na forma original a vitamina D é inativa. Sofrendo diferentes reações químicas no fígado e, posteriormente, nos rins, origina sua principal forma biologicamente ativa - o 1 α ,25-dihidroxivitaminaD₃ (conhecido como calcitriol),^[1,3] (Fig.1).

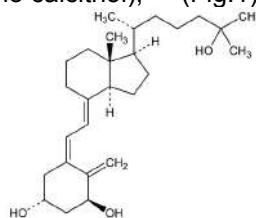


Figura 1. Fórmula estrutural do calcitriol (1 α .25-dihidroxivitaminaD₃)^[4]

Esse trabalho tem por objetivo estudos moleculares do calcitriol, analisando tanto sua geometria quanto seu espectro eletrônico de UV-Vis.

Metodologia

Fez-se análise conformacional do calcitriol usando-se Mecânica Molecular (MM). As estruturas energeticamente mais favoráveis foram selecionadas por meio da análise populacional (via distribuição de Boltzmann). Nessas estruturas, otimizou-se e obteve-se as frequências vibracionais (com B3LYP/6-31G(d)) para fases gasosa e em solvente (etanol). Esse modelado através de SMD. Calculou-se os espectros de UV-Vis usando a teoria TD-wB97XD/6-311++G(2df,p), considerando-se os dez estados eletrônicos singletes de menor energia. Na validação da metodologia, considerou-se dados de espectros disponíveis na literatura.^[4] Todos os cálculos foram realizados por meio do programa Gaussian16 (Rev. A.03).^[5]

Resultados

Os cálculos de MM do calcitriol forneceram doze estruturas energeticamente mais favoráveis, dentre mais de cinco mil possíveis. A partir de cálculos de otimização e frequência com DFT obteve-se quatro estruturas mais relevantes, sendo as mesmas para ambas as fases. Em fase gás, a estrutura **01** contribuiu com 48,07%, já em solvente, foi a **02** com 51,11%. A Tabela 1 mostra resultados de cálculos no nível de teoria TD-wB97XD/6-311++G(2df,p).

Tabela 1: Análise populacional, via distribuição de Boltzmann, em fase gás e em solvente (etanol).

GÁS			SOLVENTE (ETANOL)		
Contrib. (%)	EE (u.a.)	Estrut.	Contrib. (%)	EE (u.a.)	Estrut.
17,36	-1279,80734	02	2,71	-1279,84842	05
23,95	-1279,80765	03	9,05	-1279,84955	03
25,71	-1279,80771	01	32,37	-1279,85076	01
32,09	1279,80706	05	55,87	1279,86127	02

Observa-se maior contribuição da estrutura **05** (fase gás) e intensificação da contribuição da **02** (em etanol). Isso mostra o efeito do solvente nas estruturas de calcitriol. Os espectros de UV-Vis, ponderados a partir das contribuições das diferentes estruturas conformacionais, estão descritos na Figura 2.

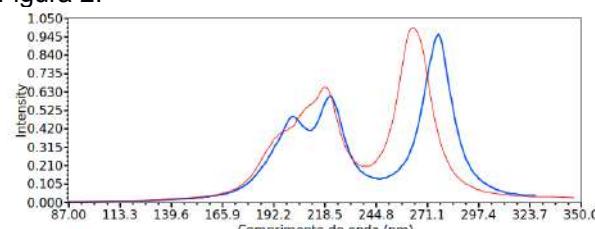


Figura 2. Espectro eletrônico de UV-Vis calculados para o calcitriol em fase gás (vermelho) e em solvente (etanol) (azul).

Observa-se que o maior pico em fase gás foi em 263,57 nm, com deslocamento do pico de ~13 nm na presença de etanol, resultando em 277,01 nm, comparado ao valor experimental de 264 nm.^[4] Os orbitais moleculares referentes a essa transição eletrônica devem-se ao HOMO e ao LUMO (Fig. 3).

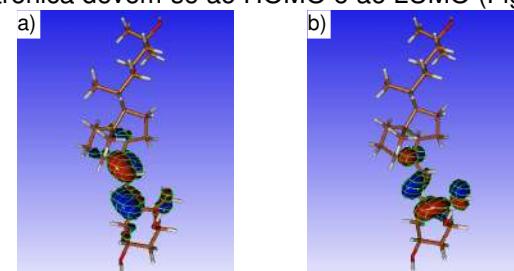


Figura 3: Orbitais moleculares associados a transição mais intensa (~277 nm) da estrutura 02 do calcitriol (55,87 %) em etanol. a) HOMO b) LUMO.

Conclusões

Conclui-se que a presença do solvente etanol reflete em deslocamento do espectro eletrônico. Ressalta-se que estudos futuros serão feitos com foco na interação do calcitriol no receptor VDR.

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Single-atom Formic Acid Dehydrogenation Catalysis

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Keywords: Heterogeneous Catalysis, Hydrogen, Formic Acid

Introduction

One of the main challenges that sciences face currently is the energy paradigm. With the exhaustion of fossil fuels and the looming reality that is the climate changing, the development of new ways to alter the current energy matrix is imperative. Current developments on renewable energy sources shows us that localized, small-scale applications still need a lot research. Hydrogen is pointed out as the most promising alternative for this issue.

Hydrogen is obtainable through sustainable means, and it does not generate greenhouse gas emissions upon combustion, while it has very high energy density, yielding 120 kJ g⁻¹. The storage of hydrogen is still a bottleneck because it is both very energy inefficient and dangerous due to its high volatility and low condensation temperature of -253 °C.

A way to circumvent the challenges of hydrogen storage is through the dehydrogenation of formic acid. The formic acid is liquid at ambient temperature, not toxic, stable, renewable, is a common byproduct of many industry applications and can be dehydrogenated.¹

The dehydrogenation reaction on copper surfaces is still not clear² and the aim of this work is to understand the first step of the interaction between the formic acid and doped copper surfaces.

Methods

DFT calculations with periodic boundary conditions were carried out in Quantum Espresso 6.2.1 in order to predict adsorption of formic acid on catalyst surfaces. The research is focused around the single-atom catalysts, with either a platinum atom or a palladium atom on a copper surface. For the calculations at hand, the formic acid molecule was placed 2 Å away from the copper slab, placed with the carboxyl oxygen close to the single-atom of platinum or palladium.

The DFT calculations were performed upon a (2x2) slab, with 4 layers of copper atoms. The pw91 and pbe functionals were used in this work. The crystallographic constants *a* and *b* were set to 10.8961 Å. The kinetic energy cutoff was set to 40 Ry for wavefunctions and ten times as that for charge density and potential and the convergence threshold was set to 10⁻⁶. K points were set to (4 4 1) for the pwscf, and (8 8 1) for the density of states (DOS) calculations.

Results

Adsorption energy was estimated through the DFT results for each case, with different functionals and different single-atom substitution. In the case of platinum with the pw91 functional, it was found to be 1.2 eV.

The DOS results for the single platinum substitution and the structure utilized for the calculations can be seen on Figure 1. Our results show how the presence of Pt modifies the valence band close to the Fermi level, suggesting its relevance in the reactivity of the doped material.

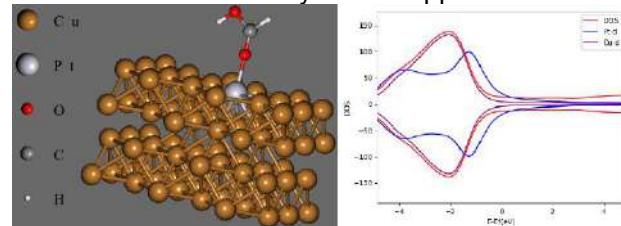


Figure 1: DOS and structure for one of the calculations.

Conclusion and Outlook

The doped copper surface seems to display a strong adsorption energy to the formic acid, possibly due to the larger d-band found on the platinum and palladium.

Single-atom catalysis shows promising results in regards to increased catalytic activity and selectivity for the formic acid reactions. Understanding how the doped surface interacts with formic acid needs further analysis, especially in different steps in the dehydrogenation reaction.

Acknowledgements

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Funcionais de troca e correlação no estudo do LaMnO₃

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Palavras-Chave: DFT, funcionais, perovskitas

Introdução

Dispositivos eletroquímicos e fotoeletroquímicos tem se mostrado atraentes nos últimos anos para aplicações em conversão e armazenamento de energia.¹ Nesse contexto, óxidos de estrutura perovskita, tais como o LaMnO₃, tem se mostrado como candidatos em potencial para desenvolvimento de catalisadores nesses dispositivos. Um dos métodos mais utilizados no estudo de propriedades dos materiais é a Teoria do Funcional da Densidade (DFT), cuja eficiência está intrinsecamente ligada ao funcional de troca-correlação empregado para estudo dos sistemas. No presente trabalho, diferentes funcionais de troca-correlação foram empregados para estudo do LaMnO₃, descrevendo suas propriedades estruturais, eletrônicas, dielétricas e elásticas.

Metodologia

A fase ortorrômbica (grupo espacial Pnma) do LaMnO₃ foi estudada por cálculos DFT utilizando o programa CRYSTAL17, utilizando os funcionais B3LYP, PBE0, PBESOL0, HSE06 e WC1LYP, considerando o efeito do uso de correções de dispersão de Grimme (D3). Os cálculos empregaram conjuntos de bases do tipo gaussiana, o fator de convergência estabelecido para os ciclos SCF foi 10⁻⁷ Hartree aliado a uma rede Monkhorst-Pack definida como 8x8x8.

Resultados

Todos os funcionais empregados apresentaram resultados em concordância com os parâmetros de rede para o LaMnO₃ obtidos por abordagens experimentais.² O funcional B3LYP apresentou um erro relativo percentual acumulado de 3,46% para os parâmetros de rede da estrutura cristalina. Ademais, os outros funcionais apresentaram erros maiores na determinação dos valores de a e b, mas erros menores na predição do parâmetro de rede c. Contudo, o erro acumulado observado para tais funcionais é superior ao valor encontrado para os cálculos usando o B3LYP. Além da descrição estrutural do LaMnO₃, o bandgap para o material também foi calculado e comparado a valores experimentais (1,7 eV)³. O funcional B3LYP também apresentou os melhores resultados, uma vez que obteve um bandgap de 1,85 eV e, consequentemente, um erro relativo percentual de 8,85%. Por sua vez, os funcionais PBE0 e PBESOL0

também superestimaram os valores de bandgap, enquanto que os funcionais HSE06 e WC1LYP obtiveram valores menores do que o valor reportado experimentalmente. Em termos de tempo de cálculo, observa-se que o custo computacional cresce na ordem WC1LYP < B3LYP < PBESOL0 < HSE06 < PBE0, sendo que o menor tempo de cálculo registrado foi de 67 minutos enquanto o maior foi de 135 minutos. Essas análises são muito importantes para que seja escolhido o funcional que melhor descreve o sistema estudado com bom custo-computacional. A correção de dispersão de Grimme (D3) foi aplicada nos funcionais e observou-se que esta aumenta o erro relativo observado para os parâmetros de rede a e b, enquanto diminui para o parâmetro c e para o bandgap. Sobretudo, o tempo de cálculo também aumenta drasticamente, tornando inviável o uso de tal correção devido ao alto custo computacional. No caso das propriedades eletrônicas, a estrutura de bandas e densidade de estados foram determinadas, evidenciando o caráter semicondutor do material. As propriedades elásticas do material foram avaliadas por meio do estudo de valores de Bulk Modulus, Shear Modulus e Young Modulus. Por fim, as propriedades dielétricas do material foram avaliadas juntamente com o índice de refração em diferentes direções.

Conclusão

A eficiência dos funcionais de troca-correlação na predição das propriedades do LaMnO₃ foi investigada. Ademais, as propriedades eletrônicas analisadas evidenciam o potencial do material para aplicação como catalisador.

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Agradecimentos

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Fragment based analysis of charge transfer excitons: insights into the structure-property relationship

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Keywords: *Organic solar cells; charge-transfer excitons; density functional tight binding.*

Introduction

The formation of interfacial charge-transfer (CT) excitons is believed to mediate the charge separation in organic solar cells. The experimental data suggest that different exciton dissociation mechanisms would be relevant, involving both high-energy (hot) and low-energy (cold) CT states. We explored a prototypical organic heterojunction comprising fullerene acceptors and dual-band donor polymers comprising thiophene (T), benzothiadiazole (BT), and benzotriazole (BTz) subunits. We considered several interface models varying the size, relative positions and orientations of the donor and acceptor domains (see Figure 1).

Methods

The electronic excitation spectra were obtained with the time-dependent long-range-corrected density-functional tight-binding (LC-TD-DFTB) method [1], and the excited states were analyzed with the fragment-based one-electron transition density matrix [2]. The CT excitons were then characterized according to their size, localization, intensity, and energy distribution.

Conclusions

The complexes with edge-on orientation were found to have denser spectra of low-energy CT states compared to the complexes with face-on orientation. The edge-on orientation would thus favor dissociation following relaxation to cold CT excitons, while the dissociation of hot excitons would be favored by the face-on orientation. The size and degree of charge transfer of the low-lying CT states also tend to be larger in the interface models with edge-on orientation. Finally, we found that larger excitons are produced by the delocalization of the electrons perpendicularly to the donor:acceptor interface. The results reported in this talk were published in a recent paper [3].

Acknowledgements

This work was supported by FAPESP (grant number 2018/22948-0) and CNPq (grant number 304571/2018-0). The calculations were performed at CNAPAD/SP, AGUIA/USP and MesoCentre at the Aix-Marseille University (France).

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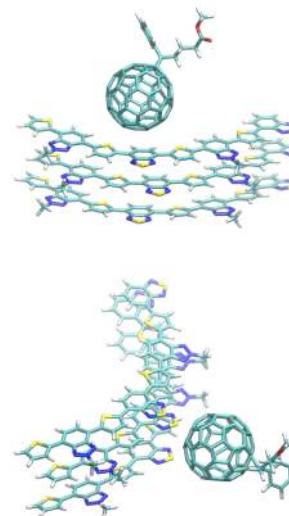


Figure 1. Models for donor:acceptor interfaces with face-on (top) and edge-on (bottom) orientation. The acceptor is composed of stacked oligomers of T, BT and BTz subunits, while the acceptor is a fullerene (PCBM) unit. The sulfur atoms are indicated in yellow, oxygen in red, nitrogen in deep blue, carbon in light blue, and hydrogen in white.

Interaction of imidazolium cations-based ionic liquids with mordenite. An ONIOM-DFT study

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Keywords: ONIOM-DFT, ionic-liquids, mordenite.

Introduction

Maintaining the actual reduction in greenhouse gas emissions must not achieve the “1.5°C targets” of the Paris Agreement. Accordingly, an imminent climate catastrophe calls for clean energy transformations, such as H₂ production and storage (HPS), and a pollution decrease, e.g., by using CO₂ and H₂S capture, storage and utilization (CSCSU) [1,2]. Tackling these issues requires the development of new materials at an unprecedented pace. Therefore, we would expect that combining imidazolium cation-based ionic liquids (Im-ILs) with zeolites a class of materials with exceptional capacities for CSCSU and HPS technologies might be obtained. In this work, we present an ONIOM-DFT study of the Im-ILs interaction with protic mordenites (H-MOR) to evaluate the capacities of these new materials of type-[BMIm]-MOR for eventual applications in HPS and/or CSCSU.

Computational Procedure

All calculations were carried out by using the GAUSSIAN-2009 software and an ONION (ω B97X:PM6) methodology. We study the ionic exchange process (IE) from H⁺ to [BMIm]⁺ only in the Brønsted acid site (BAS) located on the position T4O10 inside the 12-MR channel (M-T4-O10-H).

Results

Scheme 1 shows the thermodynamic pathways for the [BMIm].[Cl] interaction within the pores of the H-MOR (i.e., the [BMIm]⁺ adsorption inside of the H-MOR the H-MOR to produce the [BMIm]-MOR material). These pathways lead to the IE of H⁺ by [BMIm]⁺ on T4O10 position (M-T4-O10-[BMIm]). The red pathway describes the M-T4-O10-[BMIm] formation via non-covalent adsorption of [BMIm].[Cl] on M-T4-O10-H. The blue pathway describes the M-T4-O10-[BMIm] formation from an ionic mechanism that involves the deprotonation of BAS (DP) and ion-pair dissociation of [BMIm].[Cl] (i.e., the inverse process to the ion-pair formation, IP). Afterward, via IP, the M-T4-O10⁻ interacts with [BMIm]⁺ to produce M-T4-O10-[BMIm], and, simultaneously HCl is released. The M-T4-O10-[BMIm] formation via IP is a more exoergic process than via NC, and it is clear that the ionic mechanism describes the M-T4-O10-[BMIm] formation. The ΔE_{IE} value of -46.3 kcal mol⁻¹ indicate that the M-T4-O10-[BMIm] formation via IE is a highly exoergic process, so it could be expected that [BMIm]⁺ penetrate into H-MOR. The most probable sites for [BMIm].[Cl] interaction outside of the H-MOR to produce the [BMIm]-MOR material are surface silanol groups (-SiOH). Conversely to the M-T4-O10-[BMIm] formation, our results reveal that the M-T4-

O10-[BMIm] formation is a slightly exoergic process. So, no energetic or steric limitations are found to obtain the penetration of the [BMIm]⁺ inside H-MOR.

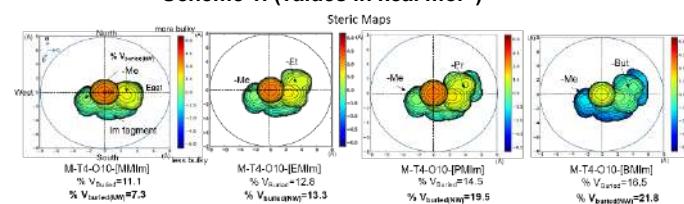
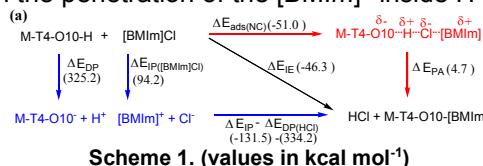
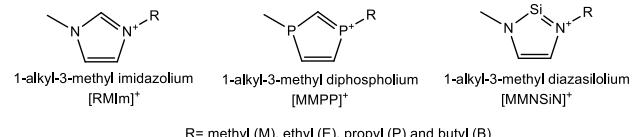


Figure 1. Steric maps for the new M-T4-O10-[Im] materials studied.



Scheme 2. Alternative cation fragments ([M]⁺) proposed in this work.

Conclusions

No significant differences in the ΔE_{IE} values for the [RMIm]⁺ studied were found (from -46.3 to -48.9 kcal mol⁻¹, see the [RMIm]⁺ in Scheme 2), but a growing steric effect produced by the alkyl chain is observed in the north-east quadrant. This could negatively affect the diffusion of H₂, CO₂ and H₂S (Figure 1). It was found that the IE of [M]⁺ (see Scheme 2) is promoted by high values of ΔE_{IP} (-132.2; -136.7 and -161.3 kcal mol⁻¹, for [MMIm]⁺, [MMPP]⁺ and [MMNSiN]⁺ respectively). We found the correlation proposed by Joseph et al. [3] between the ΔE_{IP} values with the changes in the molecular electrostatic potential (ΔV_{min}) during the interaction between M-T4O10⁻ and [M]⁺ ($\Delta E_{IP}=1.05\Delta V_{min}+28.80$, $r^2=0.968$). The adsorption energies (ΔE_{ads}) of H₂, CO₂ and H₂S on the M-T4-O10-[Im] are in the range of van der Waals non-covalent interactions, meanwhile ΔE_{ads} for M-T4-O10-[MMPP] and M-T4-O10-[MMNSiN] in the range of chemical adsorption instead.

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Escaneamento de potenciais sítios catalíticos em nanopartículas de Pt_{13-n}Ni_n (n = 0, 3, 6, 9, 13) para a reação de deslocamento gás-d'água.

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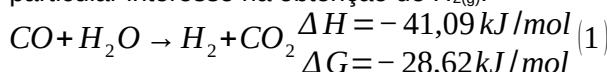
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Keywords: WGSR, Catalyses, Nanoparticles .

Introdução

O H_{2(g)} destaca-se por ter a água como produto de sua combustão. A reação de deslocamento gás-d'água (WGSR) ilustrado na equação 1 é um processo exotérmico reversível e espontâneo¹ de particular interesse na obtenção de H_{2(g)}:



Apesar de ΔH e ΔG apresentarem valores negativos, o uso de catalisadores é indispensável para que a reação ocorra sob regime cinético viável industrialmente. A utilização de nanopartículas bimetálicas de PtM (M = metais do bloco d) como catalisadores apresentam diversas vantagens, como alta atividade química, além de não ser suscetível a oxidação em presença de água^{1,2}. Visando reduzir o custo do catalisador de Pt e buscando atenuar suas características indesejadas, acrescenta-se Ni para a formação de uma liga bimetalica de PtNi. Este estudo tem como objetivo identificar quais das diferentes composições de nanoligas de PtNi podem atuar como catalisadores para a WGSR.

Metodologia

Neste estudo foram utilizados ferramentas computacionais de baixo custo, em específico os

métodos semiempíricos da família GFN-xTB³. Já os mecanismos reacionais foram construídos empregando um algoritmo de *nudged elastic band* (NEB) implementado pelo grupo de pesquisa..

Resultados e Discussão

A partir dos perfis energéticos presentes nas figuras A-I é possível observar que há a tendência de diminuição de energia conforme a dopagem por Ni aumenta. A nanopartícula de Pt₁₃ apresentou duas barreiras energéticas onerosas (25 kJ/mol e 40 kJ/mol). Mas ao ser dopada com 3 átomos de Ni, esta apresentou uma diminuição de energia reacional em termos gerais, com apenas uma etapa onerosa (40 kJ/mol). Embora a última nanopartícula, Pt₇Ni₆, também tenha apresentado uma redução de energia sua última etapa possuir um alto valor (60 kJ/mol).

Conclusão

De acordo com os perfis energéticos e estruturais, destaca-se que a nanopartícula de Pt₁₀Ni₃ apresentou o caminho reacional com menor número de etapas energeticamente onerosas.

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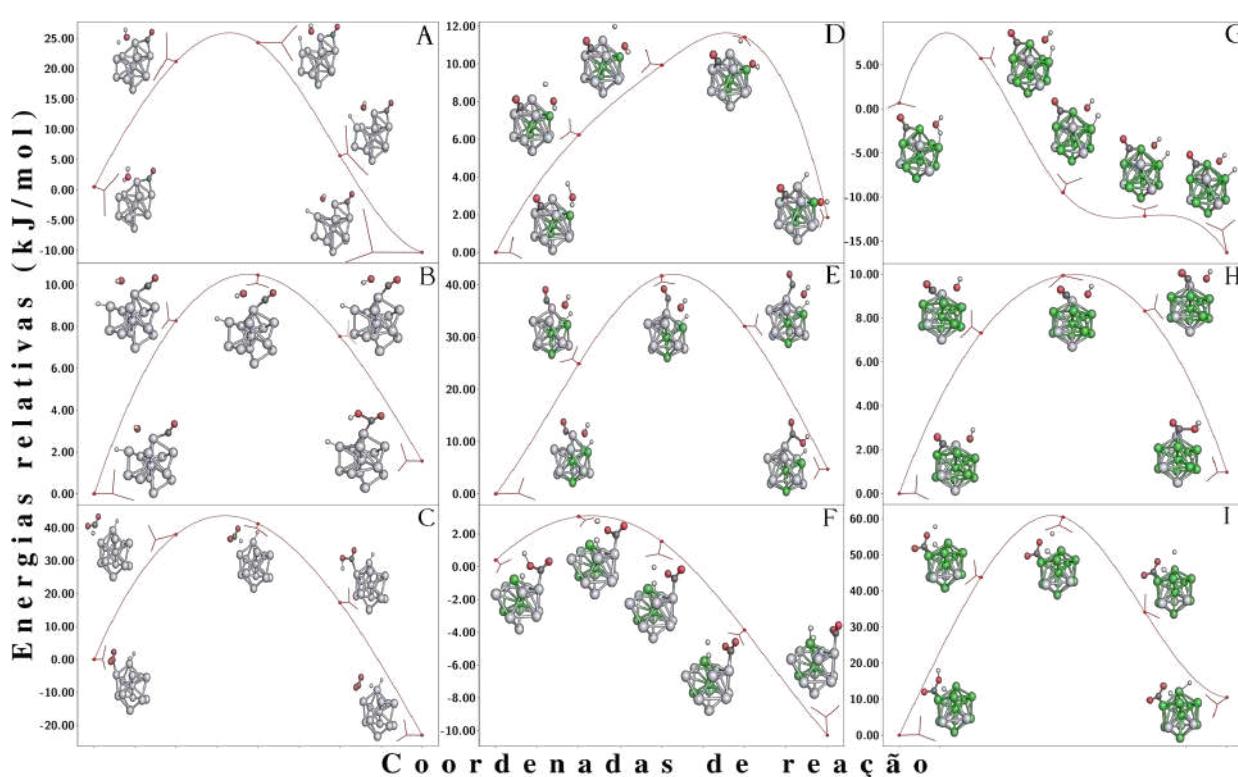


Figura 1: Figura 1: Mecanismos da nanopartícula Pt₁₃(A- Lise H₂O; B- Formação COOH; C – Formação H₂); Mecanismos da nanopartícula Pt₁₀Ni₃ (D- Lise H₂O; E- Formação COOH; F – Formação H₂); Mecanismos da nanopartícula Pt₄Ni₉ (G- Lise H₂O; H- Formação COOH; I – Formação H₂). <https://proceedings.science/p/130808?lang=pt-br>

Vanadium complex of bis(maltolato)oxovanadium (IV) as an inhibitor of β -amyloid: new force field and validation

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Keywords: force field, molecular dynamics, vanadium complexes

Introduction

Besides being insulin mimetic agents, vanadium complexes of bis(maltolato)oxovanadium (IV) (BMOV) (Figure 1) are reported as potential agents against β -amyloid-related diseases, such as Alzheimer's disease. Studies have shown that BMOV is a good inhibitor of β -amyloid ($A\beta$), which might lead to the reduction of apoptosis of neuronal cells¹. Molecular dynamics simulations are crucial steps to investigate the structure of complexes like this. Since very little information about force field parameters of metallic complexes are available, it is essential to emphasize the importance of studies that provide more information about such molecules to assist in further drug design studies. Thus, this work aims to develop a new AMBER force field for BMOV, a drug that might affect $A\beta$ aggregation.

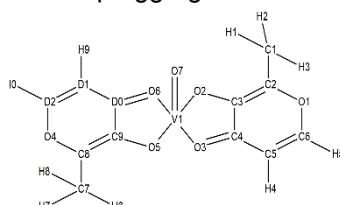


Figure 1. Structure of bis(maltolato)oxovanadium (IV).

Methodology

Initially, the global minimum energy structure was found through quantum-mechanical calculations, using B3LYP/def2-TZVP level of theory. Relativistic effects for BMOV were calculated using the spin-orbit zeroth order regular approximation (ZORA). The calculation of Restrained Electrostatic Potential (RESP) atomic charges and Hessian matrix were carried out using the same functional and basis set. Using the Paratool plugin, available from the software VMD (Visual Molecular Dynamics), the values of force constants for the bonded terms were obtained. Based on the General AMBER Force Field (GAFF) values, Lennard-Jones parameters were assigned for all atoms, except vanadium. An MD simulation in vacuum was performed, at room temperature ($T=300$ K) and total simulation time of 20 ns, using AMBER11 simulation package. Lastly, a comparison among the structural data set, experimental values² and a quantum reference was made.

Results and Discussion

When evaluating the data presented on Table 1, it is possible to conclude that the new force field, obtained

by the methodology exposed in last section, successfully described the system under study, when compared with the experimental values and the quantum reference. Furthermore, the mean of the error obtained was equal to 4.24% for bonds lengths and 2.89% angles.

Table 1. Comparison of selected bond lengths (Å) and angles (°) of two different references (experimental values and DFT) and molecular dynamics. Standard deviation values are presented in parentheses.

Atom Type	Exp. ²	DFT	New Force Field
V1-O2	1.971(8)	1.973	1.952(1)
V1-O3	1.998(8)	2.054	2.014(1)
V1-O5	1.958(8)	1.973	1.953(1)
V1-O6	2.024(8)	2.054	2.012(1)
V1-O7	1.596(7)	1.571	1.566(1)
O3-V1-O2	82.5(4)	80.1	82.2(1)
O3-V1-O6	146.8(3)	150.4	130.1(3)
O3-V1-O7	107.0(5)	104.8	110.1(3)
V1-O2-C3	108.1(7)	113.9	108.9(1)
V1-O3-C4	112.9(8)	112.4	107.4(1)

From the RMSD graph (Figure 2), it is possible to observe that during the last 10 ns, the structure under study oscillated around 1.5 Å.

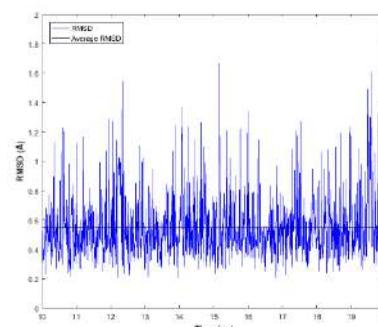


Figure 2. RMSD vs. time graph calculated for vanadium (IV) complex in vacuum.

Conclusions

The new force field parameters obtained for molecular dynamics simulation showed to be in good agreement with experimental data and a quantum reference.

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Revisitando a estrutura eletrônica do $[\text{Co}(\text{CN})_6]^{3-}$

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Palavras-Chave: Complexos; Estrutura eletrônica; Espectro eletrônico, Acoplamento vibrônico.

Introdução

Uma das classes de compostos contendo ligações carbono-metal mais simples é a dos cianocomplexos $[\text{M}^{n+}(\text{CN})_x]^{(x-n)-}$. Dos principais usos recentes do $[\text{Co}(\text{CN})_6]^{3-}$, destaca-se o uso como eletrodo na fabricação de baterias de íons de lítio,¹ e como absorventes para radionuclídeos de metais alcalinos e alcalinos-terrosos.² Nesse trabalho pretende-se revisitá-lo a estrutura eletrônica desse complexo com métodos computacionais mais atuais, oferecendo uma descrição mais detalhada dos seus estados, dos efeitos de acoplamento vibrônico que influenciam nos espectros, bem como das forças de oscilador óptico (FOO) das transições entre esses estados. Pela literatura, sabemos que o espectro eletrônico do $[\text{Co}(\text{CN})_6]^{3-}$ apresenta uma banda de maior intensidade em torno de 200 nm, atribuída à uma transição de transferência de carga (TC) metal-ligante,^{3,4} e duas outras centradas no metal em 311 ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$) e 259 nm ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$) de menor intensidade, sendo esta encoberta pela banda de TC.^{3,4} É possível ver, ainda um pequeno ombro do lado da banda em 300 nm atribuído a transição do tipo $^1\text{A}_{1g} \rightarrow ^3\text{T}_{1g}$.⁵

Metodologia

A geometria foi otimizada pelo método DFT/PBE0. O estudo dos estados eletrônicos foi feito usando TD-DFT/PBE0, CASSCF/NEVPT2 e MC-RPA, todos usando a base def2-TZVP. Foi feita, ainda, um estudo de acoplamento vibrônico através de um método já descrito na literatura⁶. Os programas usados foram o Gaussian 09 e o Orca 4.2.1.

Resultados

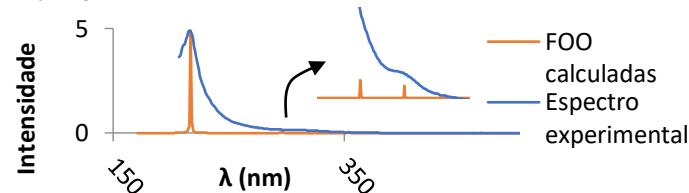
Os resultados das energias, vistos na Tabela 1 mostram que para as bandas envolvendo estados centrados no metal, a melhor descrição foi obtida pelo método NEVPT2, revelando um caráter multiconfiguracional do complexo. Esse resultado é esperado uma vez que envolve um metal da primeira linha de transição, os quais se sabe que apresentam esse caráter. No entanto, a energia da transição TC foi mais bem descrita pelo TDDFT, apesar de esse ser um método que não descreve muito bem essas transições e, diferente do que é reportado na literatura, ela apresentou caráter ligante-metal. Em todos esses métodos, as FOO das transições verticais foram nulas, conforme esperado pelas regras de seleção que proíbem transições entre estados de mesma paridade.

Tabela 1 - Energias das transições eletrônicas.

Comp. Onda (nm)	TD-DFT (nm)	NEVPT2 (nm)	MC-RPA (nm)
311	323,2	319,3	323,2
259	266,8	251,8	238,5
200	191,0	154,1	170,0

Estudos de acoplamento vibrônico conseguem prever, no entanto, as intensidades relativas dessas transições que passam a ser vibronicamente permitidas pelo acoplamento eletrônico e vibracional.

Figura 1 - Comparação do espectro simulado com o experimental. No espectro simulado foi feito um shift de 9 nm para maior λ para alinhar as bandas TC. É mostrado, também, um pequeno insert da região d-d, deslocado de 8 nm no sentido de λ para facilitar a comparação.



Nos dois espectros vemos uma transição muito intensa seguida por uma bem menos intensa. Os valores de FOO obtidas por esses cálculos mostram, ainda, que os modos de deformação angular são os que mais contribuem para o aumento da intensidade dessas transições. Essa mesma análise está sendo feita, ainda, usando o método NEVPT2.

Conclusões

Até agora pôde-se constatar o caráter multiconfiguracional das transições centradas no metal e que os modos de deformação angular são os que mais contribuíram com o aumento da intensidade por acoplamento vibrônico. Outros complexos do tipo $[\text{M}^{n+}(\text{CN})_x]^{(x-n)-}$ estão sendo estudados a fim de se definir se esse comportamento é um padrão e a razão pelo qual ele se apresenta.

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Molecular Dynamics Approach to Calculate the Thermodiffusion (Soret and Seebeck) Coefficients of Salts in Aqueous Solutions

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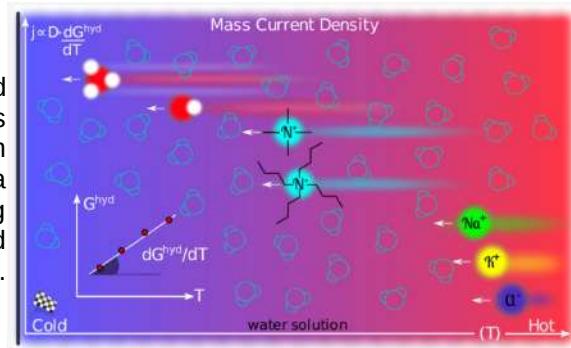
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Keywords: Soret and Seebeck Effects, Ionic Solutions, Molecular Dynamics.

Introduction

An approach^[1] to investigate the physical parameters related to ion thermodiffusion (Soret and Seebeck) in aqueous solutions is proposed herein by calculating the equilibrium hydration free energy and the self diffusion coefficient as a function of temperature, ranging from 293 to 353 K, using molecular dynamics (MD) simulations of infinitely diluted ions (K^+ , Na^+ , TMA^+ , TBA^+ , Cl^- , OH^-) in aqueous solutions. See illustration on the right.



Methodology

We have performed two types of MD simulations using the GROMACS package: (i) the conventional dynamics with the Newton equation of motion coupled with a stochastic thermostat to generate the ion–water trajectories, analyze the solvation shells around ions, and calculate the ion self-diffusion coefficient; and (ii) the stochastic dynamics with the Langevin equation of motion with a small friction constant to calculate ion hydration free energy. Several ion force field parameters were used in the simulations, and new parameters were proposed for some ions to better describe their hydration free energy.

Results

Such a theoretical framework enables the calculation of some single-ion properties, such as heat of transport, Soret coefficient, and mass current density, as well as properties of salts, such as effective mass and thermal diffusion, Soret and Seebeck, coefficients. These calculated properties were compared with experimental data available from optical measurements and showed good agreement revealing an excellent theoretical predictability of salt thermodiffusion properties (see figure on the right for Soret coefficient). Differences in single-ion Soret and self-diffusion coefficients of anions and cations give rise to a thermoelectric field, which affects the system response that is quantified by the Seebeck coefficient. The fast and slow Seebeck coefficients were calculated, resulting in values with mV/K order of magnitude, as observed in optical experiments.^[2]

Conclusion

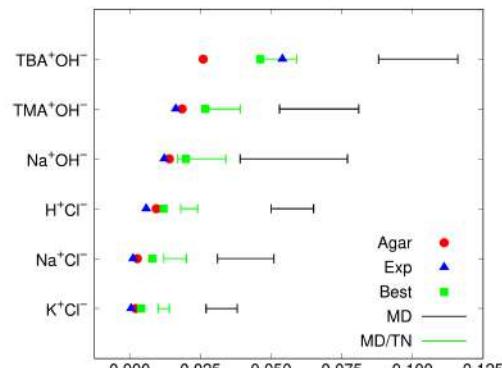
The present approach can be adopted for any ion or charged particle dispersed in water with the aim of predicting the thermoelectric field induced through the fluid. It has potential applications in designing electrolytes for ionic thermoelectric devices in order to harvest energy and thermoelectricity in biological nanofluids.

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Calculated x Experimental results for Salt Soret coefficient (in 1/K).



Hadron resonances as rovibrational states

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Keywords: *Excited hadron spectrum, orbital and radial resonances, rovibrational states.*

INTRODUCTION

The growing number of meson and baryon resonances that have been added to the Particle Data Group (PDG) [1] has stimulated research for a better understanding of the excited hadron spectrum. In this line, we developed a rovibrational model, which incorporates the semi-rigid rotor as well as the anharmonic and Coriolis corrections to describe the radial and orbital resonances of the π , K, N, and Σ hadrons [2]. Our model is similar to the one used by Pauling, in 1966, to describe Δ resonances as rotational states [3].

ROVIBRATIONAL MODEL

The vibration of the quarks and the rotation of these particles can be described by using the Pekeris solution [4] for the radial Schrödinger equation with Morse potential [5], which considers the $\hbar\omega x_e \left(n + \frac{1}{2}\right)^2$ anharmonic and $D_{rot}J^2(J+1)^2$ semi-rigid rotor corrections and includes the $\alpha_e \left(n + \frac{1}{2}\right)J(J+1)$ rovibrational coupling for states with $J > 0$. The masses of the resonances $M(n, J)$ can be calculated as (in MeV):

$$M(n, J) = D + \hbar\omega \left(n + \frac{1}{2}\right) - \hbar\omega x_e \left(n + \frac{1}{2}\right)^2 + B_{rot}J(J+1) - D_{rot}J^2(J+1)^2 - \alpha_e \left(n + \frac{1}{2}\right)J(J+1)$$

The parameter $B_{rot} = \frac{\hbar^2}{2I}$ with $I = mr^2$ was previously determined using the experimental mass and radius of the reference particle. For mesons, $r = \frac{r_E}{2}$ and for baryons, $r = \frac{r_E}{\sqrt{3}}$. The dissociation energy D and the coefficients $\hbar\omega$, $\hbar\omega x_e$, D_{rot} , and α_e are obtained by fitting the resonance masses as a function of the n radial and J orbital quantum numbers (Tab. 1).

Table 1. The D term and rovibrational parameters.

Particle	D (MeV)	$\hbar\omega$ (MeV)	$\hbar\omega x_e$ (MeV)	B_{rot} (MeV)	D_{rot} (MeV)	α_e (MeV)
π^+	725.58	464.98	22.34	1284.81	3.57	2298.17
K^+	575.41	732.50	85.22	503.02	4.70	660.93
N^+	1071.16	309.64	4.62	81.30	0.78	32.07
Σ	1361.01	197.76	12.13	80.18	1.28	32.94

RESULTS AND DISCUSSIONS

Table 2 and 3 compares the calculated π , K, N, and Σ resonances with those obtained from experiments and other theoretical predictions [6-9]. The calculated masses are found to be in good agreement with those of the experimental and other theoretical studies. Our classification is consistent with the quark model attributions for well-established resonances in the literature indicated with “•”, “***”, and “****” by PDG. In addition, we grouped resonances awaiting

confirmation indicated with “blank”, “f.” “*”, and “**”. The J^P without $\Sigma(2250)$ resonance is identified as Σ the orbital excitation with $m = 2251$ MeV and $J^P = 9/2^+$. “p.” indicates predicted states by the model.

Table 2. Experimental and calculated orbital resonances.

Hadron	Resonance	J^{PC}/J^P	Status	Mass		
				Exp.	This work	Others
π	b(1235)	1 ⁺⁻	•	1229.5±3.2	1210	1302
	$\pi_2(1670)$	2 ⁺	•	1670.6 ^{+1.0} _{-1.0}	1638	1666
	$b_3(2030)$	3 ⁺⁻	f.	2032±12	2068	1972
	$\pi_4(2250)$	4 ⁺	f.	2250±15	2240	2242
K	K ₁ (1270)	1 ⁺	•	1253±7	1247	1272
	K ₂ (1770)	2 ⁻	•	1773±8	1787	1758
	K ₃ (2320)	3 ⁺		2324±24	2315	2303
	K ₄ (2500)	4 ⁻		2490±20	2492	2498
N	N(1520)	3/2 ⁻	***	1515±5	1459	1535, 1537, 1542
	N(1680)	5/2 ⁺	***	1685±5	1736	1660, 1769, 1799
	N(2190)	7/2 ⁻	***	2180±40	2060	2045, 2150
	N(2220)	9/2 ⁺	***	2250±50	2365	2183
	N(2600)	11/2 ⁻	***	2600 ⁺¹⁵⁰ ₋₅₀	2566	2687
Σ	$\Sigma(1670)$	3/2 ⁻	***	1675±10	1678	1680, 1800
	$\Sigma(1915)$	5/2 ⁺	***	1915 ⁺²⁰ ₋₁₅	1916	1901, 2041
	$\Sigma(2100)$	7/2 ⁻	*	2146±17	2143	
	$\Sigma(2250)$	9/2 ⁺	***	2250±30	2251	

Table 3. Experimental and calculated radial resonances.

Hadron	Resonance	n	Status	Mass		
				Exp.	This work	Others
π	$\pi(1300)$	1	•	1300±100	1373	1292
	$\pi(1800)$	2	•	1810 ⁺⁹ ₋₁₁	1748	1788
	$\pi(2070)$	3	f.	2070±35	2079	
	$\pi(2360)$	4	f.	2360±25	2366	
	$\pi(2610)$	5	p.		2607	
K	K(1460)	1		1482.4±3.58	1482	1464
	K(1830)	2		1874±43	1874	1829
	K(2100)	3	p.		2095	
	N(1440)	1	***	1440±30	1550	1425, 1511
N	N(1880)	2	***	1880±50	1817	1890
	N(2100)	3	***	2100±50	2075	2089
	N(2300)	4	**	2300 ⁺⁴⁰ ₋₃₀	2323	
	N(2560)	5	p.		2563	
	$\Sigma(1660)$	1	***	1660±20	1653	1734
Σ	$\Sigma(1770)$	2	*	1770±20	1777	1739
	$\Sigma(1880)$	3	**	1880±60	1878	1751
	$\Sigma(1950)$	4	p.		1954	

CONCLUSION

The rovibrational model is useful for classifying the hadron resonances, leading to a good agreement with the experimental observations and predicting new hadron resonances. The next step is to apply the model to study other hadrons.

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Estimando a energia *full CI* a partir da distância entre a função de onda *coupled cluster* e os determinantes de Slater

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Palavras-Chave: Hartree-Fock, sistemas fortemente correlacionados, função de onda eletrônica.

INTRODUÇÃO

Atualmente a escolha do método de estrutura eletrônica é muito importante para químicos e físicos teóricos, pois através desta escolha é possível realizar cálculos computacionais precisos sobre dadas substâncias. Porém, há um gasto de tempo valioso para se definir qual método utilizar e em qual molécula. Com isso, surge a necessidade de se criar uma metodologia (ou guia) para facilitar futuras pesquisas na área, testando método por método e variando-se os sistemas a serem estudados. Um algoritmo foi recentemente desenvolvido para obter o determinante de Slater Ψ_{minD} (que minimiza a distância à função de onda correlacionada¹). As possíveis aplicações para esta função de onda estão sendo estudadas e verificamos se a integral de sobreposição de Ψ_{minD} com outras funções de onda pode ser usada para prever a energia FCI de um sistema eletrônico. O estudo foi realizado para quatro conformações da molécula H₁₀, que foi recentemente proposta como um sistema modelo para estudar a variação entre correlação estática e dinâmica².

METODOLOGIA

Inicialmente, foram calculadas as energias HF, FCI, CISD, CCSD, CCD e CID, bem como os parâmetros³ T₁ e D₁ da função de onda CCSD para a molécula H₁₀ para as distâncias interatômicas de 0,5 Å à 2,25 Å. Em seguida, com o código desenvolvido pelo grupo, foram calculadas as integrais de sobreposição (*overlap*) entre as funções $\Psi_{minD(CCSD)}$, $\Psi_{minD(CISD)}$, Ψ_{CCSD} , Ψ_{CISD} e Ψ_{HF} .

Com os resultados tabelados, fez-se uso de *Machine Learning* (utilizando o pacote scikit-learn, como descrito na referência 4) para se otimizar a dependência da energia FCI com os diferentes *overlaps* definidos acima e, com isso, obter gráficos para melhor visualização das correlações obtidas. Para se treinar a rede neural, foram utilizados os valores das energias FCI (E_{FCI}), a energia de correlação E_{corr} (E_{FCI} - E_{HF}) e o erro do *coupled cluster* (E_{FCI} - E_{CCSD}) das 4 estruturas do H₁₀. Os parâmetros da rede neural foram ajustados para cada caso, a fim de se obter ajustes precisos, mas sem *overfitting*.

RESULTADOS

Como podemos observar na figura 1, a dependência entre a energia FCI e o *overlap* $|\langle \Psi_{minD(CCSD)} | \Psi_{CCSD} \rangle|$, para conformação corrente da molécula H₁₀, é boa e pode ser prevista por uma rede neural com enorme precisão.

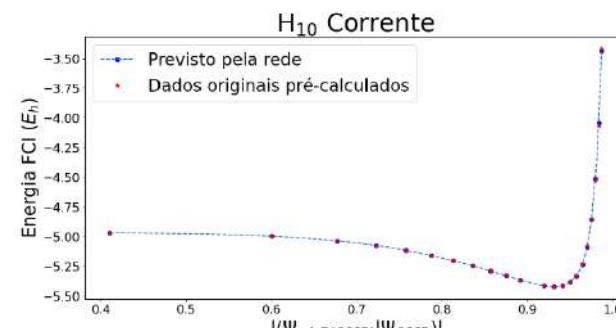


Figura 1 - Correlação entre a energia FCI com $|\langle \Psi_{minD(CCSD)} | \Psi_{CCSD} \rangle|$ do H₁₀ Corrente.

Nos outros resultados obtidos, foi possível verificar que a rede neural foi, em geral, capaz de prever como a energia FCI depende dos vários *overlaps* de maneira precisa. Houve, entretanto, resultados não satisfatórios envolvendo o *overlap* $|\langle \Psi_{minD(CCSD)} | \Psi_{HF} \rangle|$ com as 4 estruturas do H₁₀, pois não existe boa correlação deste parâmetro com a energia de correlação. Estão sendo testadas possíveis combinações de várias integrais de sobreposição e dos parâmetros T₁ e D₁, combinando, por exemplo, $|\langle \Psi_{minD(CCSD)} | \Psi_{HF} \rangle|$ com outros *overlaps*.

CONCLUSÃO

Para tal, conclui-se que a energia FCI se correlaciona bem com os *overlaps* $|\langle \Psi_{HF} | \Psi_{CCSD} \rangle|$ e $|\langle \Psi_{minD(CCSD)} | \Psi_{CCSD} \rangle|$ para a molécula H₁₀, e foi possível prever esta dependência com *Machine Learning*. Mais estudos estão sendo realizados para aperfeiçoar esta ferramenta, combinando-se vários *overlaps* para prever a energia FCI, bem como estendendo-a para outros sistemas.

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How to use geometry to optimise the Hartree-Fock wave function

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Keywords: Hartree-Fock, Optimisation, Grassmannian

Introduction

Hartree-Fock is a well-known and very important method used to optimise wave functions. Its most straightforward implementation uses the Roothaan-Hall equation and the Self-Consisted Field approach,¹ but this implementation has a couple of problems, the convergence being one of them. To solve this problem, most of the softwares use the Direct Inversion in the Iterative Subspace acceleration algorithm (DIIS)² to obtain convergence to the Hartree-Fock wave function in more cases than it is obtained in the regular implementation. However, this also does not guarantee the convergence in all cases and can be very slow to converge.

With that said, in the present work we will show how the Hartree-Fock method can be seen as an optimisation problem whose domain is a set called Grassmannian and how it is possible to use tools from a field called Differential Geometry to implement a new version of the Newton Method to optimise the Hartree-Fock wave function. It is worth to note that this method has not been well explored in the literature yet.

Methods

The first step was focused in studying the geometry of the Grassmannian as an abstract set so we could understand what the Newton Method looked like in this level of abstraction. Essentially, what happens is that we can define a real-valued function in the Grassmannian and the geometry of this space allows us to define the gradient of the function to be optimised. As it is known, the gradient is a vector that points in the direction of maximum growth of the function. So, if we take the other direction, we are minimizing the desired function. But now a question may arise: what do we consider as “taking a direction”? In the Euclidean space it is possible to consider a straight line and walk along that line, but in the Grassmannian the “straight lines” are what we call geodesics and now we walk along the geodesics. The size of each step is determined by the Hessian of the function and this is what makes our method a second-order method. In resume, we start with a point, compute the gradient of the function we want to optimise at that point, and then walk along a geodesic with the step defined by the Hessian of the function.

After that, we translated the expected value of the energy and the Slater determinants to see

how it would fit as a function defined in the Grassmannian. Explicitly, if we fix a vector space and a natural number k less than the dimension of the space, the Grassmannian is the set of all subspaces whose dimension is k . So, we can associate every Slater determinant of a system with k electrons to a subspace of dimension k and this allows us to use the Grassmannian to search for the Hartree-Fock solution. With this we have obtained a new approach to the Hartree-Fock method and now we are implementing the algorithm using the languages Python and Cython.

Results

So far we computed the gradient and the Hessian of the energy in this new language.³ One of the main problems we faced was the non-orthogonality of the basis set because every equation assumed it is orthonormal, but this is still work in progress. It is also worth to note that we have obtained for free the method called Gradient Descent, but it is a first-order method and it has not showed good convergence so far.

Conclusions

We showed how to use the geometry of the set we called Grassmannian to encode the Slater determinants and optimise the Hartree-Fock wave function using geodesics. This approach illustrates that the Hartree-Fock method is not just a variational method related to the SCF, but can also be seen as an optimisation problem in the Grassmannian. Also, since this is a second-order method, we expect to achieve better convergence than it is obtained in the regular Hartree-Fock using the Roothaan-Hall/SCF approach and, hopefully, the convergence will also be better than the approach using DIIS acceleration.

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On the structural and electronic properties of BCN diamondene

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Keywords: Diamondene; Electronic structure; 2D materials.

INTRODUCTION

New 2D materials have emerged in recent years based on diamond structures. They can be obtained experimentally from the compression of two or more layers of graphene, or similar materials, from chemical vapor deposition or hot-filament promoted hydrogenation processes [1]. Dangling bonds in diamondene are responsible for the magnetic behavior and polarized energy bands of this material [2]. The possibility to control the properties of 2D diamond materials by combining different materials such as graphene and hBN can bring motivation to the study of partial substitution of carbon by boron and nitrogen in diamondene. In this present work, we investigate, using first-principles calculations, the role of substitutional boron, nitrogen, and BN pairs, on the energetical stability, electronic structure and magnetic properties of diamondene.

Our results show which are the most favorable stoichiometries for the replacement of atoms and changes in electronic behavior of diamondene.

METHODOLOGY

Our calculations are based on the density functional theory as implemented in the SIESTA code [3]. We make use of the known exchange-correlation functional of Perdew, Burke and Ernzerhof (GGA/PBE) [4]. Spin polarization is included in all calculations. We use the norm-conserving pseudopotentials in the Kleinman–Bylander factorized form with a double- ζ basis set composed of finite-range numerical atomic pseudofunctions enhanced with polarization orbitals.

RESULTS AND DISCUSSION

The energy stability of the systems was investigated by calculating the formation energy, based on the chemical potentials of the atoms, in different environments. For both boron- and nitrogen-rich environments the most stable structures are those that present complete BN segregation in the top or bottom layer of the diamondene. The band structure and density of states of the most stable cases are shown in Figure 1(bottom). The BCN mixtures in diamondene offer a plethora of electronic structure changes providing unique behaviors in the stable structures found. Results for the most stable configuration, are shown in the figure 1(a). This result has been previously reported [5] and shows an

interesting phenomenon. It is possible to observe the metallic behavior of one of the spin components while the other presents an insulating behavior with a band gap greater than 4 eV. On the other hand, the second most stable structure (Fig. 1 (b)), all spin components show metallic behavior.

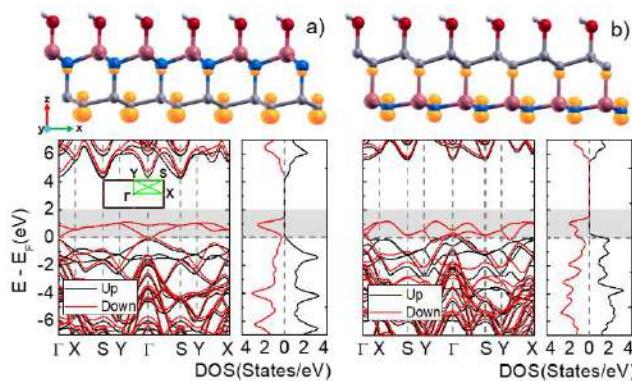


Figure 1: Local density of states, band structures and density of states of the diamondene with full segregation of (a) upper layer and (b) lower layer by BN atoms.

CONCLUSIONS

We performed ab-initio calculations of a 2x1 diamondene supercell with substitutional atoms of boron and nitrogen. In our results, we observed structures with negative formation energy, indicating an exothermic process for their formation. In the electronic properties, we observed changes in the gap and polarized spin bands, inducing electronic phase transitions, which can be useful for applications in the fields of electronics and spintronics.

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A avaliação dos parâmetros topológicos de ligações químicas não usuais.

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Palavras-Chave: *Ligações química não usuais, Química computacional, QTAIM.*

Introdução

As ligações químicas são muito importantes para entender a estrutura molecular. O modelo de Lewis é o mais utilizado para descrever ligações químicas, mas, em situações mais complexas (como conexões multicêntricas e ligações químicas não usuais) geralmente não podem ser representados por modelos clássicos. Neste caso, outros parâmetros de estrutura topológica é aplicado para a descrição de sistemas mais complexos. O objetivo principal desse trabalho é avaliar o parâmetro topológico de ligações químicas não usuais bem como obter suas estruturas de mínimo de energia para as moléculas C₂, F₂, B₂H₆ e para o cátion H₅O₂⁺ através de cálculos DFT e pós-HF.

Metodologia

A princípio foram feitos os cálculos de otimização de geometria e frequência, para as espécies inicialmente propostas e para estruturas análogas para fins de comparação de resultado. As moléculas foram primeiramente montadas no vácuo com o uso do GaussView 5.0 que foi primordial para obter os arquivos para serem usados posteriormente com o Gaussian 09.

Com as estruturas otimizadas, os próximos cálculos realizados utilizaram a Teorias dos Átomos em Moléculas (QTAIM). A partir de alguns parâmetros topológicos obtidos, foram avaliadas algumas ligações das moléculas diatônicas homo nucleares do bloco p.

Para as análises de topologia das moléculas foi utilizado Função de Localização Eletrônica (ELF) que nos dá as bacias eletrônicas associadas a agrupamentos de elétrons. O que possibilita uma investigação mais minuciosa junto ao QTAIM.

Resultados

Para C₂, todas essas indicações apontam para uma ligação dupla ou tripla, o que é consistente com a literatura e a representação de Lewis da molécula. Pode ser visto que o Laplaciano de densidade de elétrons é negativo. Igual a uma ligação covalente típica. Já para F₂ é positivo, indicando que mesmo em moléculas diatônicas homonucleares, a carga na região entre os núcleos está dispersa.



Figura 1: Bacias ELF para o F₂

Com o cátion zundel, algumas ligações não foram tipicamente covalentes por terem uma elipticidade intermediaria o que não condiz com uma ligação de hidrogênio também. O diborano formou 4 bacias em virtude dos hidrogênios e da atividade multcentrica da molécula.

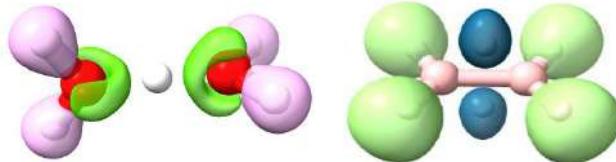


Figura 2: Bacias ELF para cátion Zundel. Figura 3: Bacias de ELF para o diborano (B₂H₆).

Para o exemplo do diborano (B₂H₆) tem-se uma ligação covalente tricentrada onde se pode encontrar através de cálculos teóricos 3 centros-2 elétrons (3c-2e). Com o uso da mecânica quântica pôde-se ter um entendimento que esses elétrons que tornam a molécula “deficiente eletronicamente” estão espalhados por todo o comprimento da mesma

Conclusões

Para F₂ que segundo a bibliografia consultada resultaria em um laplaciano negativo, contudo o valor parcialmente positivo indica uma dispersão de carga na região internuclear mesmo numa molécula diatônica homonuclear. O diborano tem a característica de ser uma ligação multi centrada, onde os elétrons percorrem e circulam por entre os dois boro e o hidrogênio central formando uma espécie de núcleo de carga movimentando esses elétrons. Para o cátion zundel as 4 bacias junto as interações eletrônicas entre as ligações oxigênio-hidrogênio centrais foram caracterizadas por uma população de 1,24; ou seja, um pouco mais fracas que uma ligação covalente usual, mas muito mais fortes do que uma ligação de hidrogênio convencional. Ademais, houve o surgimento de uma bacia de caroço para o hidrogênio central com população de 0,24.

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Infrared intensities of imaginary frequencies: Gas-Phase SN_2 Transition States

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Palavras-Chave: Infrared Intensities; Transition States; QTAIM.

Introduction: The mechanism of SN_2 reactions is well-known and taught in every introductory organic chemistry course. It consists of electron transfers from an electropositive reagent to an electronegative centre of a molecule with concerted displacement of a ligand. Following the Intrinsic Reaction Coordinate (IRC) formulated by Fukui¹, the nucleophile (Nu), approaches the electrophilic centre forming a stable complex leading to the formation of a pentacarbonyl transition state (TS). One of the atoms initially bonded to the electrophile, namely the leaving group (LG), is displaced.

The IRC path is determined by finding the only imaginary eigenvalue of the TS Hessian matrix². The same eigenvalue problem needs to be solved to determine the $3N - 6$ normal modes of vibration, with N being the number of atoms in the system. Therefore, there is a mathematical link between the chemical reaction and molecular vibrations.

In this work, the charge - charge transfer - dipolar polarization (CCTDP) model³ is applied to the TS normal mode of imaginary frequency. The partitioning of the infrared intensity in the CCTDP contributions unveils the mechanism of reaction.

Methodology: The gas phase SN_2 reaction transition state structures for nine NuCX_3LG^- systems, where $\text{Nu}, \text{LG} = \text{H, F, Cl}$ and $\text{X} = \text{H, F}$ were optimized and their normal modes of vibrations determined at the QCISD/aug-cc-pVTZ level of theory. Using Quantum Theory of Atoms in Molecules (QTAIM), atomic charges and atomic dipoles were obtained and applied to calculate the Charge – Charge Transfer – Dipolar Polarization (CCTDP) contributions to their imaginary normal mode intensities.

Following the equation of the CCTDP model, the partitioning of the infrared intensity is:

$$A_k = \frac{N_A \pi}{3c^2} \left(\frac{\partial \vec{p}}{\partial Q} \right)^2 = \frac{N_A \pi}{3c^2} (C + CT + DP)^2$$

Results: TS imaginary bands are strong, ranging from 1217 to 16086 $\text{km}\cdot\text{mol}^{-1}$, much higher than the stretching intensities found in the reactant molecules that are all less than 100 $\text{km}\cdot\text{mol}^{-1}$. For all systems, the CT contribution accounts for 63% of the total dipole moment derivative. The Charge contributions are slightly higher for transitions states where $\text{X} = \text{F}$. Dipolar polarization contributions are always small and only reflect the molecular orientation change when the nucleophile displaces the leaving group

and, therefore, they can be neglected. The same occurs for contributions from X atoms. **Figure 1** shows the contribution for each analyzed TS.

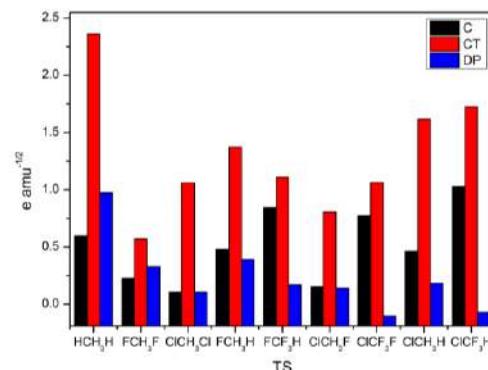


Figure 1: Charge (black), Charge Transfer (red) and Dipolar Polarization (blue) contributions to the molecular dipole moment derivative [$e \cdot \text{amu}^{-1/2}$].

To better describe the CCTDP terms, which are dependent with the spatial orientation, the systems were positioned so that Nu, C and LG are aligned with the z axis. Atomic displacements of the normal mode are represented by red arrows in **Figure 2** and indicate the IRC direction.

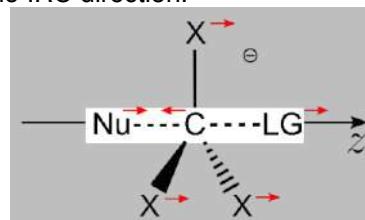


Figure 2: Positioning system utilized in all transition states. $\text{Nu} = \text{H, F, Cl}$, $\text{LG} = \text{H, F, Cl}$ and $\text{X} = \text{H or F}$.

Only atoms aligned with the reaction axis Nu-C-LG contribute to total intensity. Contributions from X are always small, and they influence only the magnitude of carbon charge term. Almost all the infrared intensities are determined by electron transfers from the nucleophile to carbon and from carbon to the leaving group. The mechanism of charge transfer revealed by the CCTDP model is consistent with the well-accepted reaction mechanism.

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AVALIAÇÃO DE FUNCIONAIS DFT NA PREDIÇÃO ESTRUTURAL DE COMPLEXOS DE Bi(III) COM LIGANTES DITIOCARBAMATOS

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Palavras-Chave: complexos de Bismuto, DFT, Ditiocarbamato.

INTRODUÇÃO

Complexos de bismuto com ligantes ditiocarbamatos têm se destacado devido as suas propriedades biológicas¹. O uso de medicamentos à base de metais tornou-se um campo proeminente e tem um papel importante na medicina atual, ajudando na prevenção e tratamentos de diversas doenças.²⁻³ Os complexos de Bi com ligantes ditiocarbamatos demonstraram boa atividade antitumoral.²⁻⁴ Esse trabalho visa a avaliação de alguns funcionais DFT na predição da geometria do estado fundamental de complexos de Bi(III) ditiocarbamatos com propriedades antitumorais.

METODOLOGIA

Foram selecionados seis funcionais DFT para avaliação: B3LYP, M06-2X, PBE, CAM-B3LYP, M06-L e TPSSh em combinação com o conjunto de base def2-TZVP e potencial efetivo de caroço (ECP). As estruturas dos complexos (Figura 1) foram otimizadas com o programa Gaussian 09 a partir dos dados de difração de raios-X.³ O desempenho dos funcionais foi obtido através de duas medidas: (i) o desvio quadrático médio (RMSD) da sobreposição entre as estruturas de raios-X e as calculadas e (ii) o desvio médio absoluto (MAD_{poly}) das distâncias de ligação entre os átomos no poliedro de coordenação.

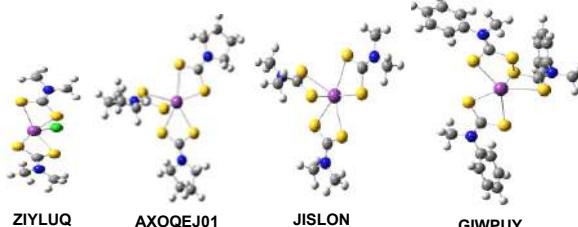


Figura 1. Estruturas de complexos de Bi selecionados.

RESULTADOS

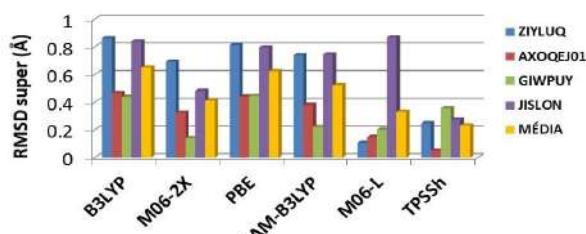


Figura 2. RMSD da superposição entre as estruturas calculadas e experimentais.

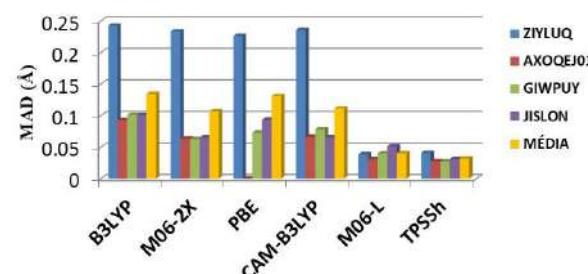


Figura 3. Desvio médio absoluto das distâncias de ligação do poliedro de coordenação MAD_{poly}.

Os resultados RMSD_{super} mostrados na Figura 2, indicam desvios menores que 1 Å para todos os complexos estudados. O funcional B3LYP apresentou o maior valor médio de RMSD 0,651 Å. O funcional TSSh apresentou valores de RMSD_{super} entre 0,05-0,30 Å, com média de 0,232 Å, sendo o mais exato. Os funcionais TPSSh e M06-L apresentaram menores valores do MAD_{poly} (Figura 3), com médias de 0,03 Å e 0,04 Å, respectivamente.

CONCLUSÃO

Os funcionais selecionados para estudo apresentam desvios considerados baixos para os complexos estudados. O funcional TPSSh se destaca como o que melhor prediz a geometria do estado fundamental dos complexos, pois apresenta os menores desvios médios. Deste modo, recomendamos este funcional para estudos subsequentes de complexos de Bi ditiocarbamatos.

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Complexos do grupo 12 com o ligante propilxantato no vácuo: Análise termoquímica, decomposição de energia e NBO

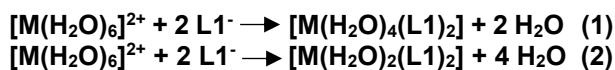
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Os xantatos (ditiocarbonatos) são compostos orgânicos que se apresentam sob a forma de ésteres ou sais e possuem o grupo -OCS₂ na sua estrutura [1]. Pesquisas recentes utilizam estes compostos na química de coordenação devido às suas diferentes possibilidades de coordenação ao centro metálico, como monodentado, bidentado e em ponte [2]. Afim de explorar estes sistemas, neste trabalho foi explorada a avaliação termoquímica dos complexos de Zn²⁺, Cd²⁺ e Hg²⁺ contendo propilxantato (L1) como ligante, assim como análises de decomposição de energia (EDA) e ligação do orbital natural (NBO).

Para a análise termoquímica foi utilizado o método M06L, a função 6-311++GG** para os átomos de S, O, C e H e a função LANL2TZ para os metais Zn²⁺, Cd²⁺ e Hg²⁺. Além disso, foram utilizadas as mesmas condições para os cálculos EDA e NBO para verificação do caráter covalente/iônico das ligações e de sua natureza. Os complexos [M(H₂O)₄(L1)₂]-C1 e [M(H₂O)₂(L1)₂]-C2 foram analisados em sua forma bidentada (**B**) e monodentada (**M**), através da substituição de moléculas de água em aquacomplexos, conforme as equações (1) e (2), respectivamente.



Além das duas diferentes formas de coordenação, foram avaliadas as diferenças energéticas dos isômeros *cis* e *trans*. A figura 1 ilustra o complexo C1 na posição *cis*.

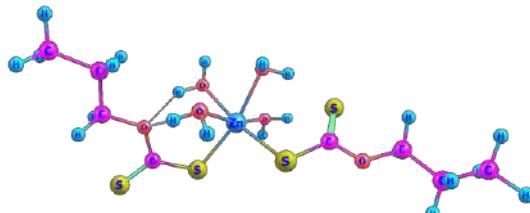


Figura 1. Estrutura optimizada do complexo C1 *cis*

A tabela 1 ilustra os valores de ΔG e NBO para as espécies *cis* e *trans* mono e bidentadas dos complexos estudados, referentes à primeira e segunda substituição. Na tabela, é possível verificar que os valores de ΔG_1 são mais negativos do que os valores de ΔG_2 , devido a uma forte interação eletrostática do ligante aniónico com o aquacomplexo

dicatiónico. Já na segunda substituição, a interação ocorre entre uma espécie monocatiónica e monoaniônica. Desta forma, a ligação M-S não apresenta um caráter puramente covalente, conforme ilustra o gráfico 1.

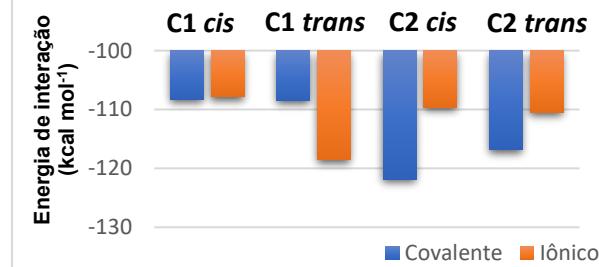
Tabela 1. Valores de ΔG e NBO para complexos de Zn²⁺ (kcal/mol)

Complexo	ΔG_1	ΔG_2	E - NBO	S(%)*
C1 M <i>cis</i>	-177,697	-104,255	202,85	p ^{91,5} s ^{8,5}
C1 M <i>trans</i>	-177,697	-104,588	122,14	p ^{98,9} s ^{0,9}
C2 B <i>cis</i>	-190,094	-99,829	144,41	p ^{92,8} s ^{7,1}
C2 B <i>trans</i>	-190,094	-100,363	134,95	p ^{93,5} s ^{6,4}
			123,59	p ^{94,2} s ^{5,7}
			149,17	p ^{92,3} s ^{7,6}

*Hibridização do enxofre coordenado ao centro metálico

O gráfico 1 ilustra o comportamento covalente/iônico das ligações M-L dos complexos C1 e C2. É possível observar que os complexos mono e bidentados possuem um caráter predominantemente iônico e covalente, respectivamente.

Gráfico 1. Caráter das ligações Zn-S(L) dos complexos C1-C2



Os valores obtidos neste estudo, confirmam a diversidade da esfera de coordenação deste ligante. Os valores de ΔG mostram uma tendência de maior estabilidade dos complexos monodentados frente aos bidentados. Isto pode ser justificado pela alta tensão do anel de quatro membros formado pela quelação do ligante ao metal. Finalmente, análise de NBO mostram que a ligação M-S ocorre pela natureza ácido-base de Lewis, com doação de densidade do orbital de caráter p do S e recepção de densidade pelo orbital s dos centros metálicos.

Agradecimentos: CNPq, CAPES, FAPERJ, PROPPi-UFF e LMQC-UFF.

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Exploring EPR Parameters of ^{187}Re Complexes for Designing New MRI Probes

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Palavras-Chave: Spectroscopic Probes, EPR, $\text{Re}(\text{CO})_3$.

Introduction

In Brazil, female breast cancer is expected to be the major cause of cancer, between 2020 and 2022, affecting over 66 thousand cases per year¹. In this scenario, early diagnosis, by using MRI techniques, is fundamental to the successful treatment of this disease. This technique is based on the NMR principles and often needs a contrast agent (CA), usually metallic complexes, to provide better images, by altering the longitudinal and transversal relaxation times². Re compounds, especially those that have the $\text{fac}-[\text{Re}(\text{CO})_3]^+$ has been studied as CA when is conjugated with the 2-(4-Aminophenyl)benzothiazole (ABT)³.

The goal of this work was study the relativistic and solvent effects on spectroscopic proprieties of the complex $\text{Re}(\text{CO})_3(\text{NNO})$ conjugated with 2-(4'-aminophenyl) benzothiazole (ReABT) (Figure 1).

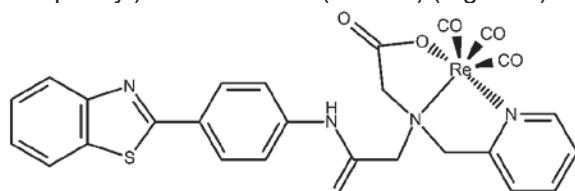
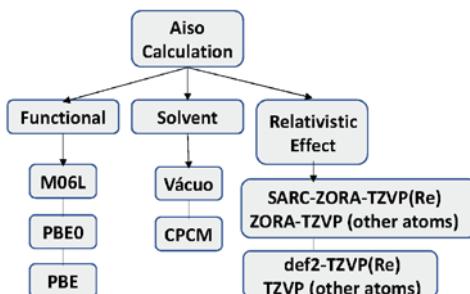


Figure 1. $\text{Re}(\text{CO})_3(\text{NNO})$ conjugated with 2-(4'-aminophenyl) benzothiazole.

Methodology

The first step of this work was to perform a geometry optimization calculation, using the DFT method, with the wB97X-D3 functional, SARC-ZORA-TZVP basis set for Re and TZVP basis set for all other atoms. Then, the DFT method was also used for calculating the A_{iso} values according the scheme 1.



Scheme 1. Methodology used for the A_{iso} calculations.

Results

First, a structural investigation has been performed and the theoretical results of bond angles and lengths was compared with experimental results obtained by Machura, 2011⁴. The major difference is in the $\text{Re}-\text{N}_{\text{ax}}$

bond, with 0.1140 Å, and the shorter between all C-O bonds, ranging from 0.0050 and 0.0090 Å. The differences in bond angles range from 0.25°, for the $\text{C}_{\text{eq}}-\text{Re}-\text{C}_{\text{eq}}$ bond, and 9.19° for the $\text{N}_{\text{ax}}-\text{Re}-\text{O}$ bond. So, we can use this geometry for further calculations, once that the results agree with experimental data. Once the geometry optimized has been obtained for the complex, hyperfine coupling constant calculations were carried out. First, the solvent effect has been evaluated on the A_{iso} values considering relativistic effects (Table 1). These results point out that, as expected, the A_{iso} value is small in solution, showing that the complex in water decrease the hyperfine coupling constant when compared to the result in gas phase.

Table 1. Hyperfine coupling constants, in MHz, for three different functionals, considering relativistic effect.

Functional	^1H	^{17}O	^{187}Re
M06L	Gas phase	2.937	96.658
	Solution	2.656	36.311
PBE	Gas phase	1.694	51.851
	Solution	1.588	24.903
PBE0	Gas phase	1.956	9.560
	Solution	1.947	9.195

Our findings also point out that the relativistic effects are necessary on ReABT A_{iso} value calculation. To define the best functional for our calculations, we compare with the experimental result for the ^{185}Re A_{iso} value, 38MHz, considering $\text{Re}(\text{CO})_3$ ⁵.

Conclusions

These results pointed out that the ReABT has potential for application as spectroscopic probe, been needed studies of the interaction in human body. Also, we can highlight that the functional M06L including relativistic effects in solution are the best methodology for A_{iso} calculations of this metallic complex.

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DFT Study of the Sequential Growth of Pd_n ($n = 1-7$) Clusters on (110D) Surface of γ -Alumina

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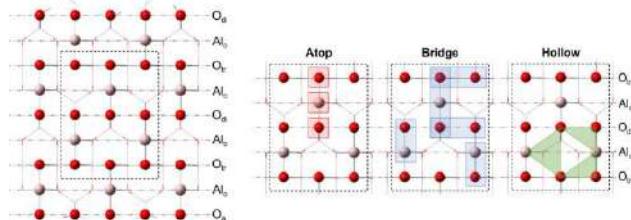
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Keywords: Pd nucleation, γ -alumina, metal–support interaction.

INTRODUCTION: The great improvement in the last decades of equipment and synthesis techniques to produce catalysts allows the stabilization of smaller and smaller metal particles on supports.¹ The catalytic performance is highly influenced by the morphology of small metal aggregates, which is in turn controlled by the magnitude of metal–support interactions (MSI).² Studies point to the existence of a competition between the MSI effect and metal–metal interactions (MMI), which direct the steps of deposition, anchoring, dispersion, nucleation, and, consequently, sintering of the metal phase.^{3,4} For these reasons, understanding how these processes occur is fundamental to the production of catalysts with higher activity, selectivity and stability. In this work we investigated the sequential growth of small Pd_n ($n = 1-7$) clusters on the (110D) surface of a γ -alumina support model.

METHODOLOGY: The $Al_{47}O_{77}H_{13}$ model was constructed based on the spinel-like lattice, the most thermodynamically stable for γ -alumina.⁵ Pd_n clusters were optimized sequentially on the (110D) γ -alumina surface (Fig. 1), starting from a single Pd atom. The most stable Pd_1 /(110D) structures, with relative energies ≤ 5.0 kcal mol⁻¹, were chosen to add a 2nd Pd atom. This procedure was repeated up to the 7th Pd atom. After obtaining a set of Pd_n /(110D) structures, a path for cluster growth was proposed (Fig. 2). Properties such as Pd–Pd distances, average adsorption energies per atom ($E_{ad(n)}$, MSI), nucleation energies (E_{nuc} , MMI) (Eq. 1, 2 and 3) and NBO atomic charges were obtained for the selected structures. All calculations were performed with the LC- ω PBE functional and the LANL2DZ (Pd) and 6-31G(d)/3-21G (γ -alumina 1st/2nd, 3rd layers) basis sets. The electronic spin states for the metal clusters were considered for the Pd_n /(110D) complexes, since $Al_{47}O_{77}H_{13}$ is a singlet. During geometry optimization only the Pd atoms were allowed to relax.

Fig. 1: (110D) surface of the $Al_{47}O_{77}H_{13}$ γ -alumina model.



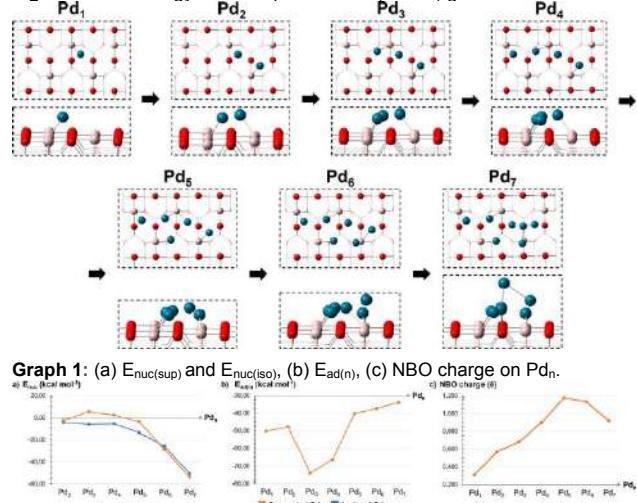
$$E_{ad(n)} = (E_{Pd_n/(110D)} - E_{Pd_n} - E_{(110D)})/n \quad (1)$$

$$E_{nuc(s)} = E_{Pd_n/(110D)} + E_{(110D)} - E_{Pd_{n-1}/(110D)} - E_{Pd_1/(110D)} \quad (2)$$

$$E_{nuc(l)} = E_{Pd_n} - E_{Pd_{n-1}} - E_{Pd_1} \quad (3)$$

RESULTS: The results point to a linear growth regime up to $n = 4$, changing to 2D in $n = 5$. The first 3D geometry has tetrahedral arrangement and arises only in $n = 7$ (Fig. 2). Up to $n = 5$, the E_{nuc} is not (or is only little) favored (Graph 1a). This energy becomes significant only after the 6th Pd, with the highest value in $n = 7$ (-53.9 kcal mol⁻¹). When the alumina coordinates are removed, the same general behavior for E_{nuc} is verified, however with more negative values up to $n = 5$. From $n = 6$ on this energy does not change in relation to the supported system. The $E_{ad(n)}$ has the same values for $n = 1$ and 2 due to the large Pd–Pd distance (3.186 Å). As this distance shortens (from $n = 3-7$, 2.981 to 2.875 Å), the $E_{ad(n)}$ decreases (-73.9 to -34.0 kcal mol⁻¹, Graph 1b). The total NBO charge on Pd_n is positive, increasing up to $n = 5$, and then decreasing until Pd_7 (Graph 1c). Such behavior indicates that while Pd anchors directly on (110D) surface, electron transfer increases. However, when Pd start to deposit away from the surface ($n = 6$ and 7), they contribute more to enhance Pd–Pd flux than the backdonation process.

Fig. 2: Lowest energy selected path for Pd_n ($n=1-7$) growth on $Al_{47}O_{77}H_{13}$.



CONCLUSIONS: The MSI seems to control the Pd_n growth up to $n = 4$, producing a linear cluster. Pd_5 is a transition point, starting a 2D regime. From $n = 6$, the MMI becomes stronger, directing the growth regime to 3D and attenuating the $Pd_n \rightarrow$ (110D) flux.

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Polímero de Impressão Molecular para o Atenolol: Um Estudo Teórico.

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Palavras-Chave: Atenolol, MIP, cálculos teóricos.

Introdução: Fármacos β -bloqueadores são drogas com efeito cardiológico empregados no tratamento da hipertensão arterial sistêmica. Dentre os β -bloqueadores mais utilizados no tratamento de hipertensão está o atenolol (ATL). O desenvolvimento de materiais adsorventes seletivos que possam ser aplicados na extração de fármacos em matrizes de interesse, a exemplo de fluidos biológicos, tem sido constantemente relatado na literatura¹. Nesse contexto, Polímeros de Impressão Molecular (MIPs) tem se mostrado uma excelente alternativa para a área da química de separações, uma vez que tais materiais podem reconhecer seletivamente o analito de interesse em vários tipos de amostras complexas. Nesse contexto, o objetivo do presente trabalho foi o de fazer uma investigação teórica inédita das melhores condições de síntese de um MIP para o ATL.

Metodologia: Foi realizada uma análise estrutural e energética por meio de cálculos DFT, em nível B3LYP/6-31G(d,p), com o objetivo de avaliar a influência da natureza de diferentes monômeros funcionais (MFs) (ácido acrílico (AA), ácido *p*-vinil benzoico (APV), ácido metacrílico (MAA) e ácido (trifluorometil-árílico (TFMAA)), estequiometrias dos complexos de pré-polimerização (CPPs) MFs/ATL, nas proporções 1:1, 1:2, 1:3, 1:4 e 1:5, bem como analisar o efeito de distintos solventes, tais como, tolueno, clorofórmio, acetona, metanol, acetonitrila, dimetilsulfóxido (DMSO) e água).

Resultados: A partir dos resultados obtidos (*Tabelas 1 e 2*) estimou-se que o melhor protocolo de síntese do MIP para o ATL empregou o APV como MF, na estequiometria 1:5 (ATL:APV)₅ e tolueno como solvente. O complexo mais estável na estequiometria 1:5 (ATL:APV) é devido a formação de 8 ligações de hidrogênio estabelecidas entre o ATL e o APV (*Figura 1*). O protocolo teórico obtido mostrou as energias de estabilização mais favoráveis para este CPP e evidenciou o papel fundamental das ligações de hidrogênio estabelecidas entre o ATL e APV na estabilidade do complexo.

Conclusão: No presente trabalho realizou-se um estudo teórico inédito, via cálculos DFT, do processo de formação de CPPs, a fim de se obter as melhores condições de síntese de um MIP para o ATL. Foi possível propor o melhor monômero funcional (APV), na melhor estequiometria (1:5) e o melhor solvente (tolueno). Este trabalho mostrou a importância da Química Computacional como uma ferramenta útil para o planejamento racional de um MIP, em nível molecular.

Tabela 1: Energia eletrônica (ΔE) e energia livre de Gibbs (ΔG) calculadas para os complexos MFs/ATL em estequiometria 1:5. Valores em kcal mol⁻¹.

Complexos	ΔE	ΔG
ATL-(AA) ₅	-61,2	-3,6
ATL-(APV) ₅	-72,6	-13,6
ATL-(MAA) ₅	-60,8	-2,9
ATL-(TFMAA) ₅	-66,2	-5,9

Tabela 2: Valores ΔE e ΔG calculadas para o complexo ATL-(APV)₅ em solventes distintos. Valores em kcal mol⁻¹.

Solventes	Complexo ATL-(APV) ₅	
	ΔE	ΔG
Tolueno	-63,9	-4,9
Clorofórmio	-59,6	-0,6
Acetona	-55,6	3,4
Metanol	-55,1	3,9
Acetonitrila	-55,0	4,0
DMSO	-54,8	4,2
Água	-54,6	4,4

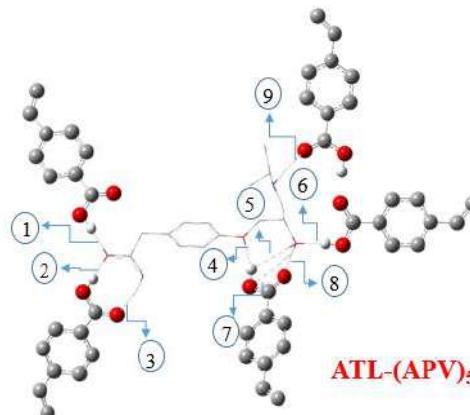


Figura 1: Estrutura otimizada do complexo mais estável ATL-(APV)₅. As ligações de hidrogênio estão representadas por números e linhas pontilhadas.

Agradecimentos: CNPq, FAPEMIG, CAPES.

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Estudo mecanístico e cinético da reação de Heck-Matsuda mediada por complexos de níquel

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Palavras-Chave: DFT, catálise, níquel.

Introdução

A reatividade superior dos sais de arenodiazônios em comparação aos haletos de arila como substratos de reações de acoplamento-cruzado^[1], somada à busca por metodologias catalíticas menos custosas na presença de complexos de níquel,^[2] resultou no estudo de uma versão da reação Heck-Matsuda mediada por complexos de níquel (HMNi) que, até recentemente, e sequer havia um protocolo experimental de sucesso reportado. Contudo, Laali e colaboradores^[3] foram capazes de obter adutos de Heck a partir 1-arilltriazenos, a forma protegida e mais estável de espécies de arildiazônio com rendimentos de bons a excelentes. Contemporaneamente com os avanços por Laali e col. nosso grupo vem trabalhando no estudo mecanístico teórico completo da HMNi visando uma reação direta entre sais de arildiazônio e olefinas alcóolicas (**Figura 1**) sem a necessidade de aplicar grupos de proteção no eletrófilo e, talvez ainda mais importante, propor uma visão mais profunda sobre a reatividade de complexos de níquel na presença de outras espécies também altamente reativas (no caso, arenodiazônios).

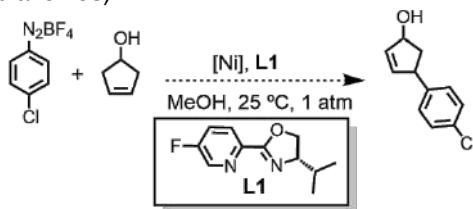


Figura 1. Reação modelo utilizada nos estudos computacionais

Metodologia

DFT/SMD-M06L. Átomos leves descritos com o conjunto de bases 6-31+G(d,p) e o pseudopotencial relativístico SDD e o conjunto de funções de bases associado, para o átomo de níquel. Energias relativas expressas em função da energia livre.

Resultados

Os ciclos catalíticos propostos para a reação HMNi ocorrendo via camada fechada singlet Ni(0)/Ni(II) ou via camada aberta dublet Ni(I)/Ni(III) foram obtidos, bem como uma análise termodinâmica da pré-catalise. A partir dos perfis cinéticos foi efetuada uma análise do span de energia^[4] que indicou que, para o ciclo singlet Ni(0)/Ni(II), a região determinante da reação muda da eliminação de hidrogênio β , para a eliminação redutiva; de acordo com a flexibilidade de rotação da olefina de partida e, principalmente, quando em presença de uma base química mais forte que o bicarbonato. O cálculo da TOF (*turnover frequency*) também foi possível e

verificamos a proximidade do valor teórico obtido com o valor experimental calculado a partir dos resultados de Laali e col.^[3] A **Tabela 1** resume essas análises. Adicionalmente, a análise termodinâmica da pré-catalise partindo de um pré-catalisador de Ni(II) permite inferir que se um radical arilo for formado *in situ* a partir do arenodiazônio, a espécie catalítica de partida para o ciclo da reação HMNi favorável será o complexo de Ni(I) L1Ni(I)Cl₂ que dará início ao caminho de reação passando pelo sistema dubleto, enquanto que na ausência da espécie radical, a formação do complexo de Ni(0) coordenado ao substrato de arenodiazônio [L1Ni(0)(ArN₂)]⁺ é favorecida sobre L1Ni(I)Cl₂ por -16,3 kcal mol⁻¹.

Tabela 1. TOF estimada (h⁻¹) e energia de ativação aparente ΔG_{ap}^* (kcal mol⁻¹) do ciclo catalítico singleto Ni(0)/Ni(II) aplicando diferentes bases químicas e olefinas.

Entr.	Base/aditivo ^c	TDI	TDTS	ΔG_{ap}^*	TOF
1 ^a	bicarbonato	Im1 β -EH	TS RE	38.3	$2,04 \times 10^{-12}$
2 ^a	carbonato	Im1 β -EH	TS β -EH	27.3	$2,28 \times 10^{-04}$
3 ^a	trietilamina	Im1 β -EH	TS RE	36.5	$4,06 \times 10^{-11}$
4 ^a	piridina	Im1 β -EH/ Im1 RE	TS RE	30.6	$5,05 \times 10^{-07}$
5 ^b	bicarbonato	Im1 RE	TS RE	34.6	$1,04 \times 10^{-09}$
6 ^b	carbonato	Im1 RE	TS RE	20.9	$1,10 \times 10^{-01}$
7 ^b	trietilamina	Im1 β -EH	TS RE	30.5	$1,06 \times 10^{-06}$
8 ^{b, c}	[BMIM](SO ₃ H)OTf	-	-	-	$2,50 \times 10^{-01}$

a) ciclopent-3-enol; b) estireno; c) TOF calculada através dos valores experimentais de Laali e col. [3].

Conclusões

A análise do span de energia para o ciclo singleto Ni(0)/Ni(II) indicou variação da região determinante da reação de acordo com a olefina de partida e a base química aplicada. O valor de TOF obtida a partir do mecanismo teórico proposto utilizando estireno como olefina e carbonato como base ($1,10 \times 10^{+01}$ h⁻¹) está na mesma ordem de grandeza da TOF calculada para os valores experimentais de Laali e col. ($2,50 \times 10^{+01}$ h⁻¹). Perfil termodinâmico da pré-catalise indica que na presença de um radical arilo a espécie catalítica de Ni ativa favorecida será o complexo L1Ni(I)Cl₂, encadeando o ciclo dubleto frente ao singlet.

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Theoretical Studies on the Cellulose – Zwitterionic Drugs Interaction by Computational Simulations.

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Keywords: Cellulose, Drug Delivery, Drug Adsorption

Nowadays different industry sectors are looking for solutions to change the usual materials by the renewable ones. For the pharmacological industry, the bio-compatibility of the final product is another crucial factor. Getting together these two needs cellulose is a key answer, and it is already used in many kinds of medicines. Recent researches show that this can go even further, cellulose-based printable devices to slow pharmacologic release¹ and disposable biosensors for medical diagnoses are a good example of that.

Besides that, the theoretical analysis of cellulose usage for medical applications still is a gap for this area. The complexity of these systems is the main barrier for that, but with the enhancement of computational methodologies, these analyses are being each day more achievable. With this in mind, we studied the amino acids adsorption on oxidized cellulose nanofibers (OCF) by classical computational simulations and quantum mechanics calculations.

Zimnitsky et. al.³ measured the adsorption properties of different amino acids in OCF aqueous solution. Among the studied drugs, tryptophan and proline stood out for being the most and less adsorbed drugs. Additionally, they also indicate that the adsorption mechanism depends on the proton transference, forming a negative charged fiber and protonating the drug molecules.

Our goal was to explain the different adsorption properties of drugs (tryptophan and proline) in the hydrated OCF, and investigate the adsorption dependence on the proton transference process.

Initially, geometry optimization of the glucose molecule (basic component of cellulose) together with the interest drug was performed with the proton bound to the glucose or to the drug. With the free energies differences, it is possible to compute the expected population of each state. The binding energy between both molecules was also computed.

Then, Molecular Dynamics (MD) simulations were performed with a system composed by one OCF with 434 glucose in crystalline structure, ~17 thousand water molecules, counter-ions and drugs molecules, using GROMOS force field, for two sets of analysis. In the first, we prepared a OCF with 40 modified groups (~50% of the total available) and 40 drugs molecules were added to the simulation box. This system was simulated in three forms: all of the drugs molecules in the zwitterionic form, all in the protonated form, and a system with half of each.

Additionally, OCF with different degrees of modification (20, 40 and 80 groups) were simulated with different quantities of available drugs (20, 40 and 80 molecules). From these trajectories general aspects of the adsorption dynamics were analyzed, such as the hydrogen bond formation, the adsorption shell structure, interaction energies, and the average number of drugs adsorbed.

The proton transference showed to be much more likely to happen on the proline interaction (66.6%) when compared to the tryptophan (0.1%). For both systems the binding energy considerably increased with the protonation. The protonation process does not interfere significantly for the tryptophan adsorption, but for the proline, the protonation of at least half of the molecules was crucial for the complete adsorption.

The adsorption of tryptophan was greater when the number of modified groups was lower than the available molecules, which happens due to the cluster formation of this hydrophobic molecule. Both drugs presented strong interaction energies of around 40kcal/mol with the fiber, representing a stable loading.

Support:

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Investigação teórica do mecanismo da reação de condensação de Knoevenagel entre compostos carbonílicos e malononitrilo.

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Keywords: Condensação de Knoevenagel, DFT, catálise

Introdução

A condensação de Knoevenagel é uma reação amplamente utilizada por se tratar de uma poderosa ferramenta sintética referindo-se à formação de uma nova ligação C-C, sendo largamente utilizada na produção de perfumes, produtos farmacêuticos e polímeros. [1-3]

Esta reação é extremamente versátil, tendo em vista que pode ser catalisada por diversos tipos de compostos com sítios ácidos e/ou básicos, possibilitando o desenvolvimento de diversos trabalhos, tanto focados na síntese e caracterização de novos compostos, quanto focados na aplicação de novos compostos que possam catalisar a reação melhorando a cinética assim como também os rendimentos dos produtos da reação. [1-3]

Diante do valor científico e tecnológico da condensação de Knoevenagel, é de extrema importância estudar as causas dos efeitos observados nos experimentos, com isso faz-se necessário o auxílio das metodologias teóricas para propor os mecanismos de reação mais prováveis que ocorrem nesta reação.

Objetivos

Estudar o mecanismo de reação da condensação de Knoevenagel entre compostos carbonílicos e malononitrilo, sugerindo os prováveis intermediários de reação bem como seus estados de transição, utilizando, para isso, a Teoria do Funcional de Densidade (DFT).

Metodologia

A DFT é aplicada através de métodos computacionais, no trabalho em questão, os cálculos envolvidos na otimização dos mecanismos da reação foram realizados no software Orca 4.0.2 utilizando o funcional PBE com o conjunto de base TZVP juntamente com o método de solvatação contínua CPCM.

Resultados

Foram testadas duas propostas de mecanismo para a reação entre o formaldeído e o malononitrilo, uma para a reação não catalisada e outra para a reação catalisada por trimetilamina, ambas com DMF como solvente. Para o mecanismo da reação não catalisada imaginou-se, inicialmente, que a condensação ocorreria com a interação exclusiva entre os reagentes, mas desta forma o produto de interesse não seria formado. Assim ficou constatado que o solvente participa da reação através da formação de dois estados de transição

(NCET1 e NCET2) sendo este o caminho de reação mais provável até o produto de interesse.

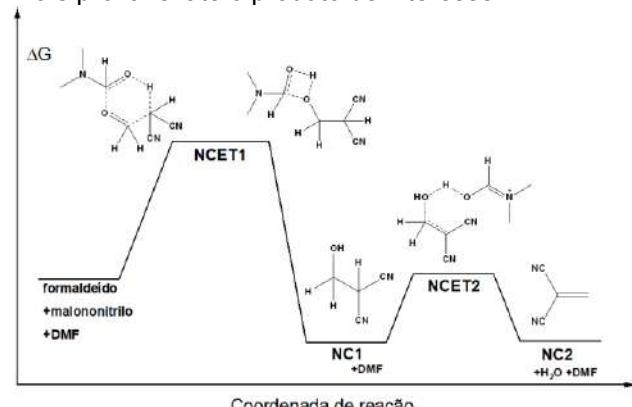


Figura 1 - Energias relativas das estruturas intermediárias no mecanismo da condensação de Knoevenagel não catalisada.

Para a reação catalisada constatou-se a formação do íon imínio (RC1) permitindo a carbonila do formaldeído ser ativada através da desprotonação do malononitrilo e, a partir de uma S_N2 (RCET1), a reação é direcionada à formação do produto de interesse.

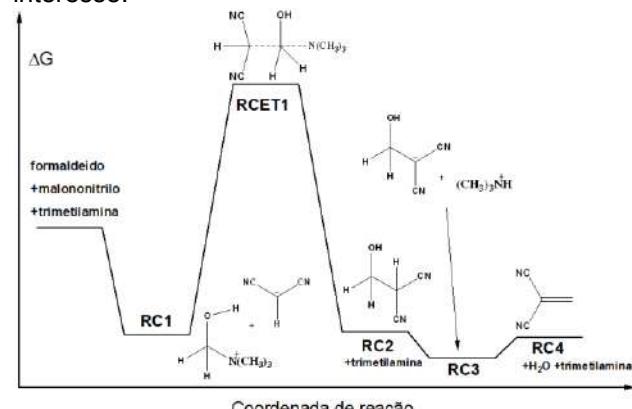


Figura 2 - Energias relativas das estruturas intermediárias no mecanismo da condensação de Knoevenagel catalisada.

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In silico study of traditional herbal as candidates to inhibit the SARS-CoV-2 main protease

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Palavras-Chave: *In silico study, herbal, SARS-CoV-2 M^{pro}.*

INTRODUCTION

COVID-19 is a disease caused by the SARS-CoV-2 virus since December 2019¹. As consequence, it was responsible for more than 4,300,000 deaths worldwide. Although ca. 4,000,000,000 vaccine doses were administered, it is important and emergent the development of drugs against COVID-19. Among the SARS-CoV-2 proteins, the main protease (M^{pro}) plays an essential role in the process of viral maturation, such that its inhibition prevents viral replication. Moreover, since SARS-CoV-2 M^{pro} is dissimilar to human proteases², it is possible to develop inhibitors non toxic. Regarding the inhibitor candidates, the traditional herbal is an interesting source of compounds due to their low toxicity and availability, minimizing possible side effects. Thus, the present *in silico* study was carried out using 4066 compounds from herbal to inhibit the SARS-CoV-2 M^{pro} .

METHODOLOGY

Figure 1 illustrates the procedure adopted here.

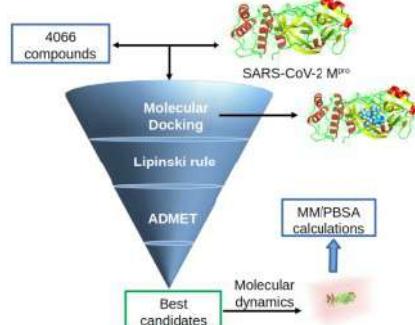


Figure 1. Schematic representation of the methodology. The virtual screening was performed with the Autodock Vina program, through docking calculations. The herbal compounds were obtained from SWEETLEAD library, and the geometry of SARS-CoV-2 M^{pro} crystallographic structure from PDB, code 6W63. The six best-docked compounds, which obey the Lipinski rule and ADMET analysis, were complexed with the M^{pro} . Then, each system was submitted to the molecular dynamics (MD) simulations in aqueous media for 50 ns, using the GROMACS package³. Finally, the binding free energy ($\Delta G_{binding}$) was calculated using the MM/PBSA method.

RESULTS AND DISCUSSION

From the virtual screening, the 16 best-scored ligands with binding energy lowest than -9.7

kcal/mol were selected. Six of them obey the Lipinski's rule (except for molecular weight) and they are not mutagenic and tumorigenic: physalin B 5,6-epoxide (PHY), methyl amentoflavone (MAM), withaphysalin C (WPC), trilobamine (TRI), cepharanoline (CEP), and tetrrandrine (TET).

Along the 50 ns of MD simulation, all complexes are stable at temperature of 310 K and the ligands keep stable into M^{pro} active site, as showed in Figure 2.

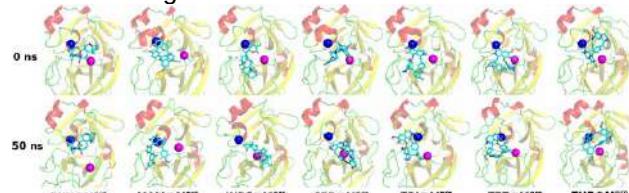


Figure 2. Snapshots at 0 and 50 ns of the MD simulation for all complexes.

In Figure 1 and Table 1, it was presented the results for tubocurarine (TUB), a FDA drug approved, due to its higher similarity with CEP, TRI and TET compounds. The $\Delta G_{binding}$ presented in Table 1 show that all compounds can inhibit the M^{pro} , with the methyl amentoflavone being the most promissory.

Table 1. Energy contribution (kcal/mol) for the present complexes through MM/PBSA method.

Herbal	$E_{van der Waals}$	$E_{electrostatic}$	$E_{polar solvation}$	E_{SASA}	$\Delta G_{binding}$
PHY	-47.4 ±0.2	-34.5 ±0.4	39.4 ±0.3	-4.94 ±0.02	-47.4 ±0.3
MAM	-49.8 ±0.2	-49.1 ±0.7	49.2 ±0.3	-5.30 ±0.02	-55.1 ±0.4
WPC	-27.8 ±0.2	-35.6 ±0.5	28.8 ±0.2	-3.50 ±0.02	-38.1 ±0.4
CEP	-43.1 ±0.2	-19.7 ±0.2	32.0 ±0.3	-4.78 ±0.01	-35.7 ±0.3
TRI	-57.9 ±0.2	-22.4 ±0.2	33.1 ±0.1	-5.54 ±0.01	-51.9 ±0.2
TET	-66.0 ±0.2	-8.6 ±0.2	29.7 ±0.3	-6.02 ±0.02	-50.9 ±0.3
TUB	-51.2 ±0.2	-249.1 ±1.0	89.1 ±0.4	-5.90 ±0.02	-217.1 ±0.7

The lowest $\Delta G_{binding}$ value for TUB may be an artifice in the calculation due to its positive charge. The same overestimation was observed in the CEP, TRI, and TET with charge +2 (data not shown here).

CONCLUSION

In this study, six herbal compounds were selected using theoretical methods. The results indicated that they are potential candidates to inhibit the SARS-CoV-2 M^{pro} .

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Theoretical Study of CO₂ Capture in Porous Materials: ZIF-78

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Keywords: Carbon Capture, MOFs, Molecular Dynamics

Introduction

We are using molecular modeling to study porous crystal materials nanoparticles known as Metal Organic Framework (MOF). In particular, we analyzed the MOF ZIF-78 made of atoms of Zn²⁺ tetra-coordinated with the organic groups nitro- and nitrobenzo-imidazole [1] interacting with abundant atmospheric gases such as N₂, O₂, Ar, water vapor and CO₂. Thus, we analyze this MOF selectivity and capacity of CO₂ capture, the effect of humidity in this process and the influence of other abundant atmospheric gases.

Methodology

We performed quantum mechanics calculations and computational simulations with classical force fields to describe the interactions of the ZIF-78 with the gas molecules [2]. Initially, we obtained the atomic charges to characterize the ZIF-78 electronic density [3]. Then, we modified the classical force field parameters to assure the stability of nanoparticles and similarity with the crystallographic structure. Lastly, we performed simulations of the nanoparticle embedded in the gases and analyzed the internal and superficial capture.

Results

We identified that the ZIF-78 interacts more with CO₂, H₂O and N₂ than with other gases. Based on the calculated properties showed in Table 1, we observed that the CO₂ capture is more efficient than the H₂O, however the presence of humidity drastically decreases the capacity of CO₂ capture of ZIF-78. Also, we observed that in flue gases, when the proportion of CO₂ is 1 to 9 of N₂, approximately, the capture of CO₂ reduces, because of the reduction of the CO₂ partial pressure, but still is relevant and the selectivity is kept, and the interact with surface Zinc atoms is unaffected, moreover, the N₂ molecules are not captured compared to CO₂.

Conclusions

We concluded that the superficial Zinc atoms of the nanoparticle are important interaction sites with the gas molecules, and that the use of the MOF ZIF-78 for CO₂ capture must be made only with dehydrated

gases so that all of its ability can be utilized. Furthermore, due to the low CO₂ partial pressure in atmospheric gas, ZIF-78 nanoparticles is not a good composite material for CO₂ capture in atmospheric gas, but it is a very good material for CO₂ capture in post-combustion gas due to its increased partial pressure.

Table 1: Density ρ_{int} of internal captured molecules (g/cm³), interaction energy E_{surf} (kcal/mol) and the coordination N_{surf} of the gas molecules with the superficial Zinc atoms. In parentheses is the standard deviation.

Molecules	ρ_{int}	E_{surf}	N_{surf}
CO ₂	0.42(2)	-20(5)	4.2
H ₂ O	0.36(6)	-70(8)	5.0
N ₂	0.023(8)	-10(2)	2.4
Mixture (1:1)	0.12(3):0.27(3)	0:-70(8)	0:5.0
C ₂ O:H ₂ O			
Mixture (1:1)	0.42(4):0.001(2)	-20(6):0	4.2:0
C ₂ O:N ₂			
Mixture (1:9)	0.28(3):0.004(4)	-20(6):0	4.2:0
C ₂ O:N ₂			

Support

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ESTUDO DFT DA INTERAÇÃO DO FÁRMACO 5-FLUOROURACIL COM UM CLUSTER DA MOF HKUST-1

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Palavras-Chave: HKUST-1, 5-Fluorouracil, DFT.

INTRODUÇÃO

A aplicação das estruturas metalorgânicas (MOFs) nas áreas de catálise, troca iônica, adsorção, bem como no encapsulamento e liberação controlada de fármacos, fazem das MOFs matérias promissoras^{1,2}. Em um estudo experimental realizado por Lucena et al, a MOF de cobre HKUST-1 demonstrou uma boa capacidade de adsorção e um perfil de liberação lenta do fármaco o 5-fluorouracil (5-Fu)². Portanto, o objetivo deste trabalho é o estudo computacional fundamentado na Teoria do Funcional de Densidade (DFT) da interação do fármaco 5-Fu com um modelo cluster da HKUST-1, com o propósito de avaliar quais são os fatores que conduzem a adsorção e liberação controlada desse fármaco.

METODOLOGIA

O programa GaussView 5.0 foi empregado para criar o modelo de cluster Cu₂(BTC)₄ e do 5-Fu (**Figura 1**). Uma busca conformacional da interação do Cu₂(BTC)₄ com 5-Fu foi realizada a nível DFT.

As geometrias foram otimizadas a nível PBE-D3 com conjunto de base def2-TZVP para o cobre em combinação com potencial efetivo do caroço e 6-31G(d,p) para os demais elementos. Os estados tripleno e singuleto do cluster foram considerados. Todos os cálculos foram realizados com o pacote computacional Gaussian 09.

RESULTADOS

Inicialmente foi realizado um estudo conformacional para localizar a configuração energeticamente mais favorável do 5-Fu com o Cu₂(BTC)₄. As estruturas de equilíbrio dessa interação foram otimizadas a nível teórico PBE-D3/def2-TZVP/6-31G(d,p). Na **Figura 2** é mostrada estrutura otimizada do confórmero mais estável e na **Tabela 2** as energias de Gibbs relativas dos confórmeros. Observou-se que a estrutura mais estável, resulta da interação do oxigênio do grupo (NH)₂C=O com o cobre, com distância de ligação Cu-O de 2,23 Å. Além disso, a possível ligação de hidrogênio intramolecular CO…HN (1,76 Å) contribui

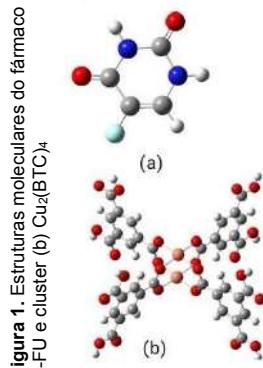


Figura 1. Estruturas moleculares do fármaco (a) 5-FU e cluster (b) Cu₂(BTC)₄

para a estabilidade do sistema. A análise da energia dos estados de spin indica que o o estado singuleto é mais estável que tripleno, **Tabela 1**.

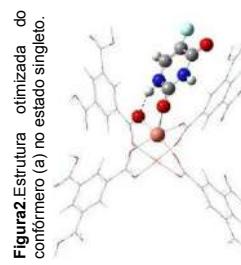
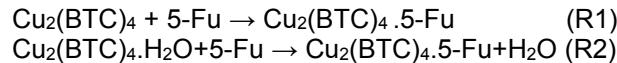


Figura 2. Estrutura otimizada do confórmero (a) no estado singuleto.

Tabela 1. Energia eletrônica e energia de Gibbs relativa (ΔG) dos confórmeros de estado singuleto e tripleno

Confórmeros	Energia eletrônica (u.a)		ΔG relativa (kJ.mol ⁻¹)	
	Singuleto	triplo	singuleto	triplo
a	-4091,66	-4091,59	0	0
b	-4091,65	-4091,58	13,25	4,13
c	-4091,65	-4091,58	15,90	8,16
d	-4091,65	-4091,58	22,47	9,12

Os parâmetros termodinâmicos para a interação do Cu₂(BTC)₄ com 5-Fu e a reação de troca da molécula de H₂O pelo fármaco em fase gasosa, foram calculados a partir das reações abaixo:



Os resultados indicam um processo de adsorção espontânea do fármaco no sítio cobre insaturado (**Tabela 2**).

Tabela 2. Parâmetros termodinâmicos para interação do Cu₂(BTC)₄ com 5-Fu e reação de troca de água, calculados para o estado singuleto em kJ.mol⁻¹.

Reações	ΔG	ΔH	$T\Delta S$
R1	-38,21	-93,11	-54,90
R2	-40,14	-54,03	-13,89

CONCLUSÃO

Os resultados sugerem que o sistema é estabilizado por interação forte entre 5-Fu e átomo de cobre do cluster e possível ligação de hidrogênio intramolecular. A energética de interação mostra um processo de adsorção espontânea e favorável à troca de moléculas de água pelo fármaco no sítio de cobre.

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The Si(³P)+SO₂ reaction and its astrochemical implications

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Palavras-Chave: silicon; astrochemistry; DFT calculation.

Introduction

In the interstellar medium, most of the silicon is fixed as silicates in grains of dust, but a relevant amount of it has been observed in the gas phase (MACCARTHY et al. 2003). Among the first detected silicon bearing species are SiS and SiO. Contrary to the well understood SiO molecule, SiS formation and reactivity is still an open research topic. In this work we investigated the Si+SO₂ reaction, which is expected to be a source of SiS (ZANCHET et al. 2018), aiming to verify if it may have an impact on the abundances of species with astrochemical interest, such as SiS, SiO, SO and others.

Methods

The reaction mechanisms have been predicted by DFT calculations at M06-2x/pcseg-2 level of theory (ZHAO, TRUHLAR, 2008; JENSEN, 2014). Geometries optimizations, zero-point energies (ZPEs), vibrational frequencies and intrinsic reaction coordinate calculations were performed using GAMESS-US (SCHMIDT et al. 1993). Additionally, MOLPRO (WERNER et al. 2015) has been used as a tool to scan the potential energy surface in search for transition states. After the initial explorations the results will be refined at the CCSD-F12 level (ADLER et al. 2007).

Results

The results show that the main products of this reaction are the monoxides SO and SiO, with an energy release of -273 kJ mol⁻¹. No favorable pathway has been found leading from SO₂ + Si to other products, which contradicts the expectation of it being a source of SiS. Furthermore, SiS is predicted to be stable in collisions with molecular oxygen. We also predict that S(³P)+SiO₂ and O(³P)+OSiS will yield SO+SiO, through a similar mechanism. The explorations revealed several potential energy minima and transition states over the triplet potential energy surface, with the tetratomic molecule SSiO₂ as the predicted global minimum.

Conclusions

According to our results the Si(³P) + SO₂ reaction exothermically yield the monoxides SO and SiO, contributing to their relative abundances in certain regions of the ISM. However, unlike expected by Zanchet et al. (2008), this reaction is not involved in SiS formation. As a contribution to the field, our calculations predicted a new possible neutral-neutral

source of SiO, to be included in astrochemical databases.

Acknowledgments

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Combinação de redes neurais e cálculo de deslocamento químico de RMN ^1H e ^{13}C como forma de avaliação estrutural do helianuol F

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Palavras-Chave: Produtos naturais, DFT, RMN.

Introdução

A combinação entre modelagem molecular e produtos naturais intensificou a discussão sobre o tema reassinalamento estrutural. Isto se deu, principalmente, devido ao desenvolvimento de novas ferramentas computacionais disponíveis para simular e avaliar parâmetros de RMN, como por exemplo, as redes neurais.¹ O helianuol F foi isolado em 1999 por Macías e colaboradores², é considerado um potencial herbicida natural e apresenta uma estrutura em que o anel aromático está fundido à um anel heterocíclico de 7 membros (figura 1). Ressaltamos que a sua estrutura foi determinada baseando-se na comparação com dados de RMN de ^1H e ^{13}C de membros da classe previamente isolados.²

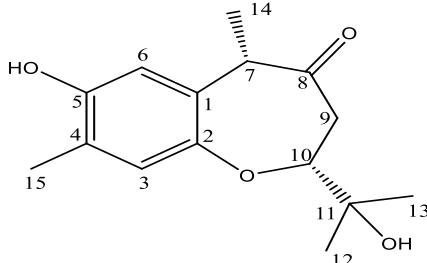


Figura 1. Estrutura do helianuol F.

De acordo com o nosso interesse na aplicação destas novas metodologias para analisar estruturas de produtos naturais, decidimos avaliar a compatibilidade da estrutura do helianuol F por meio da combinação de redes neurais e cálculos de deslocamento químico de ^1H e ^{13}C RMN com os seus dados experimentais.

Resultados e Discussão

Os cálculos de deslocamento químico de RMN de ^1H e ^{13}C para o helianuol F, realizados através da teoria do Funcional da Densidade acoplado ao método GIAO (GIAO-HDFT), em nível de teoria GIAO/mPW1PW91/6-31G(d)/mPW1PW91/6-31G(d) utilizando o pacote de software Gaussian 09³, forneceram valores de MAD e RMSD elevados, 0,26 e 0,35 (RMN de ^1H , figura 2) e 4,2 e 6,2 (RMN de ^{13}C , figura 3), respectivamente. Esses valores insatisfatórios são oriundos de erros pontuais elevados (figura 2 e 3) e indicam que pode haver uma inconsistência entre a estrutura simulada e a estrutura proposta inicialmente para o produto natural. Este resultado chamou nossa atenção e para

confirmar esta nossa avaliação inicial, aplicamos a ferramenta ANN-PRA.⁴

Desenvolvida por Ariel Sarotti em 2013, ANN-PRA é um procedimento capaz de validar estruturas, baseando-se na análise de padrões por meio de redes neurais, esta ferramenta classifica a estrutura proposta como correta ou incorreta.⁴ Dito isto, aplicamos esta ferramenta para confirmar nossos cálculos iniciais e obtivemos a seguinte resposta: "The proposed structure seems INCORRECT".

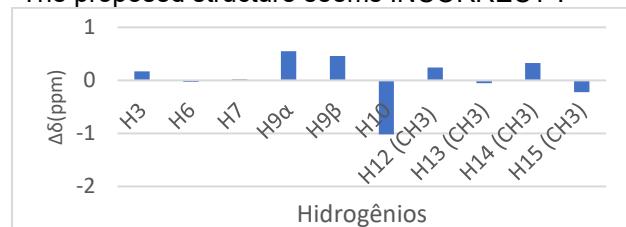


Figura 2. Comparação das diferenças dos deslocamentos químicos de RMN de ^1H do helianuol F com o produto natural isolado.

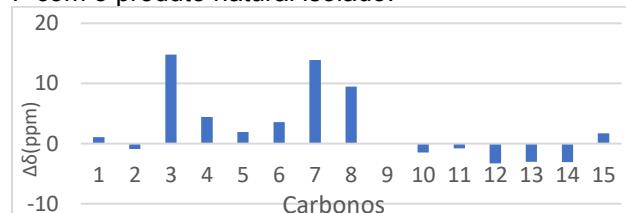


Figura 3. Comparação das diferenças dos deslocamentos químicos de RMN de ^{13}C do helianuol F com o produto natural isolado.

Conclusão

As análises realizadas indicam um possível erro estrutural no helianuol F, visto que a comparação dos dados de ^1H e ^{13}C RMN calculados com os respectivos dados experimentais do produto natural geraram valores de MAD e RMSD insatisfatórios. O uso de redes neurais com a ferramenta ANN-PRA corrobora esta proposta da necessidade de uma possível reavaliação estrutural para helianuol F.

Agradecimentos

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DFT analysis of organocatalysis with NHCs and alcohols as co-initiators in the formation of poly(δ -valerolactone)

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Keywords: Polymers, N-Heterocyclic Carbenes, DFT, ROP.

Introduction

Plastics are mostly made from fossil raw material and are one of the most important reasons for today's major environmental problems. One way to get around this is with the use of biodegradable materials, such as carbohydrates and sugars, among others.¹ An alternative is the production of biodegradable polymers in reactions using organocatalysis. Hence, N-Heterocyclic Carbenes (NHCs, Fig. 1) have been used as organocatalysts in lactone polymerization reactions (ROP), with alcohols as co-initiators.^{2,3}

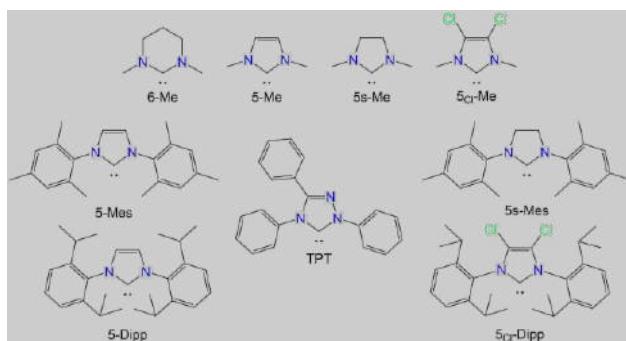


Fig. 1 - Studied N-Heterocyclic Carbenes.

Methodology

In this work, we have deployed DFT range-separated hybrid NGA N12SX functional and the triple-zeta 6-311+G(d,p) basis set to investigate the mechanism of lactone polymerization, in reactions catalyzed by NHCs, using alcohols as co-initiators. The geometries of selected stationary points were fully optimized, considering water as an implicit solvent, applying the IEFPCM model. The computed stationary points were selected based on mechanisms proposed in the literature.^{2,3} δ -Valerolactone was used as a lactone prototype.

Results

Two main mechanisms have been proposed for the ROP of lactones, one pass through a zwitterionic intermediate and the other by deprotonation of the co-initiator. Thus, from the reaction pathway simulations we had produced the main data summarized in the tables below:

Table 1 - ΔH^\ddagger values (kcal mol⁻¹) for the zwitterionic route.

ΔH	6-Me	5-Me	5s-Me	5c-Me	5-Mes	5s-Mes	5-Dipp	5s-Dipp	TPT
TS1	12,05	7,92	8,24	10,30	8,27	8,62	10,90	14,47	13,12
I1	4,12	-0,61	0,88	5,28	3,35	3,27	6,59	13,21	9,56
TS2	18,42	19,57	22,89	27,52	28,98	30,78	---	---	37,40
I2	9,51	15,19	16,58	23,83	17,18	19,86	---	---	32,63

Table 2 - ΔH^\ddagger values (kcal mol⁻¹) for deprotonation of the co-initiator route (ethanol).

ΔH	6-Me	5-Me	5s-Me	5c-Me	5-Mes	5s-Mes	5-Dipp	5s-Dipp	TPT
TS3	2,20	6,52	6,07	10,38	8,48	8,65	9,95	15,03	14,62
I3	-6,69	-1,71	-2,39	2,49	0,87	0,26	1,18	5,02	6,72
TS4	1,00	4,68	4,21	8,40	7,15	6,39	---	11,21	12,97
I4	-1,48	-2,22	-2,26	-1,92	0,00	-2,35	---	-2,05	-0,68

Figure 2 illustrates the mechanisms studied built with the computed stationary points for the two reaction paths (TS = transition structures, I = intermediates).

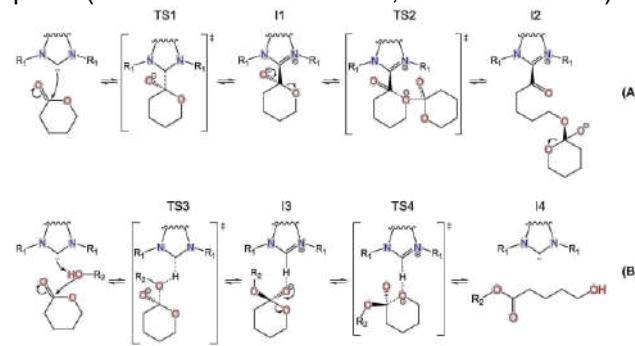


Fig. 2 - (A) Zwitterionic route; (B) Deprotonation of co-initiator route

Moreover, relative proton affinities of the NHCs were computed and compared with previous pKa studies⁴ in order to indicate the catalytic capacity of each one.

Conclusion

Therefore, with the values shown in **Tables 1 and 2**, we infer that the mechanism with participation of a co-initiator has lower activation enthalpies than the corresponding one involving a direct attack of the NHC on the lactone. In the mechanism via a zwitterion, the second step, opening of the lactone ring (TS2), has much higher energy barriers than the first one. For the mechanism involving the co-initiator, proton transfer to the NHC, concerted with a nucleophilic attack on the lactone (TS3), is the rate-determining step.

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Em busca de nanoestruturas estáveis de fluoreto de lítio

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Palavras-Chave: Lithium Fluoride, Artificial Bee Colony Algorithm, Global Minimum Structures

Introdução

Haletos de metais alcalinos são uma classe de compostos isolantes formados por sistemas com forte caráter iônico, que cristalizam em uma estrutura cúbica de face centrada (FCC) [1]. Recentemente, alótropos e pequenos aglomerados (*clusters*) de fluoreto de lítio (LiF) têm sido investigados com o objetivo de estabelecer uma relação entre estrutura e as propriedades [2].

Tais aglomerados podem conter de poucas até milhares de unidades estruturais distintas [3]. Dessa forma, é uma classe de compostos que atrai o interesse de diversos pesquisadores na produção de novos materiais devido às suas propriedades que divergem daquelas do seio do sólido (*bulk*). Podem ser empregados na construção de dispositivos ópticos miniaturizados, como guias de onda [4], micro cavidades [5] e lasers moleculares [6].

Neste trabalho realizamos a busca do mínimo global de estruturas de $(\text{LiF})_n$ ($n=10-24$), utilizando o método de *Artificial Bee Colony Algorithm*, para uma triagem inicial de possíveis candidatos, seguida de cálculos DFT (Teoria do Funcional da Densidade) para as estruturas selecionadas estruturas.

Metodologia

A busca por estruturas de mínimo global (MG) dos aglomerados de $(\text{LiF})_n$ foi realizada utilizando o algoritmo *Artificial bee colony* implementado no software ABCluster [3,7] para $n = 10-24$. O potencial de Born-Mayer combinado com a interação de Coulomb (CBM) de dois corpos foi aplicado na busca de todos os MGs.

As estruturas de baixa energia foram selecionadas para posterior otimização de geometria e cálculo de frequências vibracionais harmônicas utilizando DFT. O funcional foi escolhido com base em resultados anteriores para esse sistema [2]. As famílias de *clusters* foram analisadas com base na sua estrutura, estabilidade relativa entre os vizinhos e energia de ligação.

Resultados

A triagem realizada utilizando o ABCluster foi eficiente para obter estruturas de baixa energia de

aglomerados pequenos conforme confirmado pelos posteriores cálculos quanto-mecânicos. Porém, com o aumento do tamanho do sistema, sua acurácia em obter estruturas estáveis diminuiu.

Conforme o tamanho do aglomerado aumenta, é possível observar uma convergência na direção da formação de uma estrutura FCC. Porém, também foram observadas estruturas do tipo nanotubo que possuem uma maior estabilidade relativa em relação aos seus vizinhos.

Conclusões

Foi possível observar uma vasta riqueza estrutural conforme o número de unidades estruturais de LiF aumenta, abrangendo estruturas desde a FCC até estruturas do tipo nanotubo e nanogaiolas.

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Cálculo do valor energético de suplementos proteicos por métodos semiempíricos

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Palavras-Chave: termoquímica, semiempírico, suplemento proteico.

Introdução

Nas últimas décadas, o avanço das metodologias teóricas e da computação fez a Química Computacional (QC) se destacar entre as metodologias que investigam os fenômenos químicos. Como isso, vários artigos têm mostrado que a QC pode ser utilizada como uma ferramenta educacional visando facilitar a aprendizagem e aumentar o interesse dos alunos nas disciplinas de química em cursos de graduação^{1,2}.

Esta aula experimental teve como objetivo introduzir a QC na disciplina de Química Orgânica II do curso de Engenharia de Alimentos da UFAPE e trabalhar com cálculos termodinâmicos relacionados aos aminoácidos e carboidratos presentes em suplementos proteicos (SP).

Os softwares utilizados no trabalho foram o Avogadro³ e o Mopac⁴. Os métodos semiempíricos (AM1, PM3, PM6, PM7 e RM1) foram utilizados devido aos seus menores tempos computacionais.

Metodologia

Inicialmente, foi realizado uma aula para introduzir alguns conceitos sobre QC e apresentar os softwares utilizados no experimento.

As estruturas moleculares foram construídas e pré-otimizadas utilizando o Avogadro. Os inputs do Mopac foram preparados baseados nas palavras-chave disponível no manual do programa (<http://openmopac.net/manual/index.html>).

Resultados

De acordo com a Tabela 1, o método PM3 apresentou valores de entalpia de formação (ΔH_f) dos aminoácidos mais próximos dos valores relatados na literatura⁵.

Tabela 1: Fatores de correção das ΔH_f .

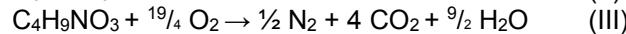
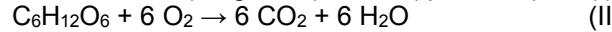
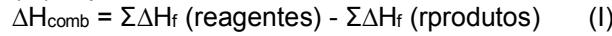
Métodos	Fator de correção ^a
AM1	0,9278
PM3	0,9989
PM6	0,9669
PM7	0,9501
RM1	1,0322

^a média dos resultados de (ΔH_f experimental/ ΔH_f literatura)

Além de aminoácidos, os suplementos proteicos também possuem carboidratos que, para fim dos cálculos computacionais, foram representados pela glicose ($C_6H_{12}O_6$).

As entalpias de combustão (ΔH_{comb}) da glicose e dos aminoácidos foram calculadas a partir dos valores de

ΔH_f obtidos pelo método PM3 (I). Os produtos da combustão da glicose foram assumidos como CO_2 e H_2O (II) e, no caso dos aminoácidos, N_2 , CO_2 , H_2O (III) e, para os aminoácidos contendo enxofre, o SO_3 .



A partir dos valores de ΔH_{comb} , da composição em massa do SP e das massas molares (MM) dos aminoácidos e da glicose (Tabela 2), os alunos calcularam o valor energético experimental do SP e, comparando com o valor energético do rótulo, observaram um erro percentual de 6,6%.

Tabela 2: ΔH_{comb} e valores energéticos (VE) da glicose e de alguns aminoácidos presentes no SP.

	ΔH_{comb} (KJ/mol)	MM (g/mol)	massa (g/30g de SP)	VE (KJ/30g de SP)
treonina	-1709,07	119,1	1,73	24,82
serina	-1183,49	105,09	1,22	13,74
alanina	-1332,56	89,08	1,22	18,25
histidina	-2636,98	155,14	0,45	7,65
prolina	-2223,11	115,12	1,46	28,19
glicose	-2235,59	180,16	5	62,04
total _{exp}				453
total _{rótulo}				485

O valor energético total do experimento (total_{exp}) da Tabela 2 foi calculado pelo somatório dos valores energéticos da glicose e dos 17 aminoácidos presentes no SP (ácido aspártico, treonina, serina, ácido glutâmico, alanina, valina, isoleucina, leucina, tirosina, fenilalanina, histidina, lisina, arginina, prolina, cistina, metionina e triptofano).

Conclusões

Neste experimento foi possível relacionar diversos conteúdos de química (estereoquímica, cálculos estequiométricos e termoquímica) e aplicar a QC como uma metodologia ativa de ensino. Além disso, a comparação dos resultados com as informações nutricionais do SP possibilitou a contextualização da QC com a Engenharia de Alimentos.

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Estudo *ab initio* da estrutura eletrônica de complexos com ligante 1,2-ditiolato

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Palavras-chave: CASSCF, DLPNO-CCSD(T), 1,2-ditiolato.

Ligantes 1,2-ditiolato ficaram conhecidos por exibir propriedades supercondutoras a nível molecular. Estas estruturas possuem propriedades químicas interessantes devido à possibilidade de se obter estruturas planas e conjugadas e à presença de átomos de enxofre na estrutura que são extremamente polarizáveis. A presença destes átomos permite a estes ligantes se relacionarem com metais em diversos estados de oxidação por estabilizá-los¹. O estudo dos processos eletrônicos usando métodos modernos de cálculo apresentados neste trabalho busca contribuir na elucidação desta classe de compostos quimicamente ricos.

O trabalho consistiu no estudo de ânions complexos de Bi(III) (**1**), Sb(III) (**2**), e Cu(II) (**3**) com dois ligantes 1,2-ditiolato (Figura 1). Os compostos foram otimizados com teoria do funcional de densidade (DFT) usando PBEh-3c. Primeiro, foram feitos cálculos com a análise *Fractional Occupation Number Weighted Density*³ (FOD) para detectar correlação estática. Segundo, foram realizados cálculos *Complete Active Space Self Consistent Field* (CASSCF) associado ao *N-electron Valence Perturbation Theory* (NEVPT2) para avaliar caráter multirreferencial e multiconfiguracional e determinar a estrutura eletrônica. Em terceiro, foi feito um estudo DLPNO-CCSD(T). Por fim, cálculos de espectro UV por TDDFT com o funcional duplo-híbrido DSD-BLYP. Os resultados foram obtidos com o software ORCA e funções de base Def2-TZVP.

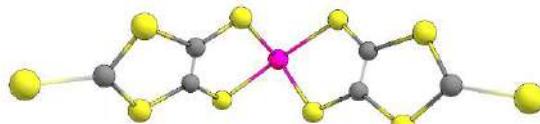


Figura 1: Estrutura do $[M(dmit)_2]^{x-}$. ●-S; ●-C; ●-M,x = Sb,(1); Bi,(1) e Cu,(2).

Segundo os dados FOD, o composto (**3**) possui maior correlação eletrônica estática do que as demais. O que provavelmente se deve à presença de um elétron desemparelhado nos orbitais d do cobre capaz de interagir com outros elétrons de orbitais d próximos em energia (< 0,1 eV).

As três estruturas do trabalho não apresentaram caráter multirreferencial ou multiconfiguracional segundo os cálculos CASSCF/NEVPT2 feitos com a sugestão FOD. O estado fundamental das três estruturas possui uma configuração eletrônica fortemente predominante, superior a 90%. Os primeiros estados excitados mostram natureza

multiconfiguracional. Transições duplamente degeneradas ocorrem devido à simetria dos sistemas. O NEVPT2 indica relevante presença de correlação dinâmica com correções variando de 0,1 até 1,0 eV para cada estado.

Os dados DLPNO-CCSD(T) indicam forte estabilização por interação eletrostática e por meio de correlação dinâmica. A presença do enxofre (altamente polarizável) no ligante torna a ligação com o centro metálico com grande caráter covalente, confirmado pela transferência de carga dos ligantes para o metal - ordem de 2,7 eV para (**1**); 2,3 eV para (**2**) e 0,8 eV para (**3**).

Os espectros calculados com TD-DFT assemelham-se ao experimento^{1,3}, exceto para desvios por efeito solvente em transições calculadas acima de 900 nm com baixa força do oscilador. Os valores corroboram os dados CASSCF e DLPNO-CCSD(T) (Tabela 1), exceto para a transição M←S do cobre. As transições eletrônicas partem simetricamente dos dois ligantes com pares de estados excitados próximos em energia.

Tabela 1: Bandas (nm) do espectro UV-VIS dos complexos estudados obtidas por TD-DFT.

Transição	1	2	3
M←S	500-510 (525-565)	450-480 (300-400)	650-780 (500-600)
$\pi \rightarrow \pi^* C=S$	580-600 (425-500)	540-600 (400-500)	500-600 (400-500)
$\pi S_m \rightarrow \sigma^* M-S$	390-405 (450-480)	450-480 (450-480)	-

Teórico (experimental)

Os complexos de Bi(III), Sb(III) e Cu(II) com 1,2-ditiolato possuem natureza multiconfiguracional em seus estados excitados com o estado fundamental isolado. As estruturas possuem forte correlação dinâmica, conforme visto por DLPNO-CCSD(T) e correções NEVPT2 ao CASSCF. Os resultados TD-DFT apoiam a presença de correlação eletrônica pela forte deslocalização dos elétrons nos ligantes e excitações aos pares nos espectros.

Os autores agradecem ao suporte dado pelo FAPERJ, LMQC-UFF, NACAD-UFRJ e CNPQ.

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UNIDIMENSIONAL DOPED DIAMOND-LIKE-CARBON MODEL

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Key words: DLC, doped, electric properties.

INTRODUCTION

Diamond-Like Carbon (DLC) is a material consisting of C-H bonds of great interest to the technology industry, having very interesting physical and chemical properties such as: high wear resistance, chemical stability, high mechanical hardness and low friction coefficient. DLC is a metastable form of amorphous carbon that contains a significant fraction of sp^3 -type bonds¹.

The so-called doped DLC are materials in which the insertion of atoms other than C and H in their structure takes place. When inserted, dopants are able to change the structural properties, influencing both their microscopic and macroscopic properties. Studies, mainly experimental, on the influence of different dopants are found in the literature as in²⁻⁴.

METHODOLOGY

A study on the variation between the microscopic properties of undoped and doped DLC in 1-D system was carried out. The dopants used in this work were aluminum, boron, chromium and titanium. Bond lengths and angles, dipole moment (μ), quadrupole moment (θ), polarizability (α), zero-point energy (ZPE) and GAP energy. The calculation were carried out using B3LYP/aug-cc-pVDZ with GAUSSIAN09⁵.

RESULTS

Figure 1 present the doped DLC_1D model DLC. The doped molecule was inserted in the middle of the system. Initially we use a model with nine carbons, or eight and one doping atom. Table 1 shows geometric parameters for undoped and doped DLC system with different atoms (X), while in Table 2 presents the electric properties. There is little difference in the CC, CH distance and HCH, CCC, HCC angle, meaning the dopant atom does not affect the CH chain, but the geometric parameters as CX, XH distance, CXC and HXH are different according with X atoms.

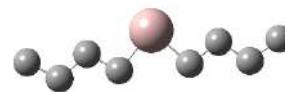


Fig.1: Doped DLC_1-D model.

Tab. 2: Values of μ , α , θ , ZPE e E, for different dopants.

	μ [D]	α [a.u.]	θ [D Å]	ZPE [kcal mol ⁻¹]	GAP [eV]
DLC	0.098	118.828	109.970	170.7	7.95
B	1.647	153.470	106.636	163.6	3.79
Cr	2.461	161.784	127.949	156.1	5.18
Al	2.408	181.937	120.306	158.0	6.23
Ti	1.557	160.664	132.375	156.5	4.83

Chromium as doping has higher influence in the electric properties, such as dipole and quadrupole moments, aluminum presents the higher polarizability but the undoped DLC has the higher GAP energy.

CONCLUSION

Different dopants changes the electrical properties of the system, the GAP energy can be 7.95 eV for the undoped system to 3.79eV for the boron doped one. According to the film application doping them, we can change their properties according our interest.

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INPE, CAPES, FAPESP

Tab. 1: Lengths, bond angles and distances between atoms for different dopants.

	R _{CX} [Å]	R _{XH} [Å]	R _{CC} [Å]	R _{CH} [Å]	A _{HCH} [°]	A _{CCC} [°]	A _{HCC} [°]	A _{CXC} [°]	A _{HXH} [°]
DLC	1.533	1.103	1.533	1.102	106.03	113.33	109.29	113.62	106.04
B	1.731	1.211	1.548	1.100	107.18	111.94	109.52	94.01	114.87
Cr	1.941	1.580	1.540	1.102	106.41	112.93	109.35	118.73	92.60
Al	2.138	1.601	1.549	1.100	106.91	112.42	109.41	88.71	118.07
Ti	2.058	1.726	1.540	1.101	106.18	113.06	109.31	108.27	113.73



Predicting Rate Coefficients at the Complete Basis Set Level

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Palavras-Chave: complete basis set, variational transition state theory, CH₄+O₂

Introduction

Methods for extrapolation of the electronic energy to the infinite basis limit (CBS) have been proposed in order to avoid errors in the prediction of reaction energy differences and barrier heights. Despite the known exponential dependence of rate coefficients on critical energies, studies assessing the quality of CBS models related to accuracy in predicting rate coefficients cannot be found.

Thus, this work aims to promote the computational implementation of five CBS mathematical models, in order to calculate rate coefficients for the CH₄+O₂→CH₃+HO₂ reaction, the main responsible for the initiation of methane combustion, to compare rate coefficients obtained through conventional and variational Transition State Theory (CTST and VTST) and to assess the role of CBS corrections of the electronic energies in such calculations.

Computational Methods

Geometry optimizations and reaction paths were obtained at the M06-2X level with aug-cc-pVDZ and aug-cc-pVTZ basis sets. Single point calculations were performed at the MP2 level with the aug-cc-pVXZ (X=T,Q,5) basis sets and at the CCSD(T) level, with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, in order to perform the extrapolation to complete basis set utilizing the CBS procedure, making use of a FORTRAN language software developed at our laboratory.

$$\text{model 1: } E(n) = E^\infty + c_1 \exp(-c_2 n)$$

$$\text{model 2: } E(n) = E^\infty + A n^{-3}$$

$$\text{model 3: } E(n) = E^\infty + A n^{-3} + B n^{-5}$$

$$\text{model 4: } E(n) = E^\infty + A (n + 1/2)^{-4} + A (n + 1/2)^{-6}$$

$$\text{model 5: } E^\infty = E_L + a \left| \xi(4) - \sum_{\ell=1}^L \ell^{-4} \right| + b \left| \xi(6) - \sum_{\ell=1}^L \ell^{-6} \right|$$

KCVT software was used to calculate rate coefficients, at six different temperatures, through VTST and CTST. Skodje & Truhlar tunneling corrections were also applied to the CTST rate coefficients.

Results

Starting from the stationary points located at the M06-2X/aug-cc-pVDZ level, CBS model 5 led to the best agreement of the VTST rate coefficient with experimental data. For CTST rate coefficients, with

and without tunneling correction, model 3 was the best performing for the accurate calculation of rate coefficients.

Starting from the stationary points located at the M06-2X/aug-cc-pVTZ level, model 5 led to the smallest deviations between calculated (VTST and CTST, with and without tunneling correction) and experimental rate coefficients.

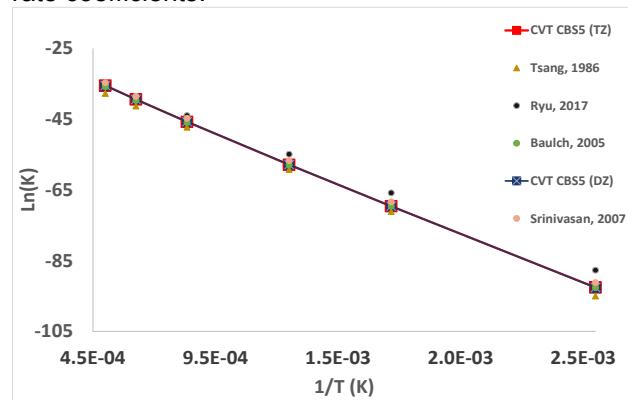


Figure 1: Arrhenius plots showing predicted and previously reported rate coefficients.

It is notorious, that there are no explicit differences among the CBS-corrected rate coefficients obtained from calculations performed with the DZ or TZ basis sets. The most considerable absolute deviations among the calculated and experimental rate coefficients are observed by comparison with the results reported by Ryu, ranging from 2.97 to 4.8 for T < 1000 K and 0.24 to 1.77 for T > 1000 K.

Conclusion

Results suggest model 5 as the most effective CBS method for predicting barrier heights and rate coefficients. It can also be inferred that, for related combustion reactions, it is possible to perform a more accessible basis set and still reach a rigorous result. It is also important to emphasize the effectiveness of the variational method, which, even without quantum tunneling correction, achieved smaller absolute deviations compared to the results obtained via the conventional method, even when corrected.

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DFT studies of an oxalate-bridged oxidovanadium(IV) binuclear complex with an anti-diabetic activity

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Keywords: Oxovanadium(IV), Broken-Symmetry, Spin Density

Introduction

Recently, the centrosymmetric oxidovanadium(IV) complex with formula $(Et_3NH)_2[\{VO(OH_2)(ox)\}_2(\mu-ox)]$ (**V₂**), was synthesized and characterized by single crystal X-ray diffraction and spectroscopic analyses.¹ The anti-diabetic activity of **V₂** was evaluated in HepG2 cells, showing an effect comparable to that caused by insulin in hyperglycemic media. We present herein Density Functional Theory (DFT) studies, and their comparison with the experimental data.

Methods

Calculations were performed using the ω B97XD functional and the def2TZVP basis set available in Gaussian16². The optimized geometry of the isolated anion of **V₂** was calculated using the crystallographic data as an initial guess. The molecular optimization was performed firstly in vacuum and then in a simulated water environment through the conductor-like polarizable continuum model (CPCM) approach. Atomic charges were calculated using Bader scheme through Multiwfn 3 code. Frontier orbitals were rendered by Chemcraft 1.8. The broken symmetry approach³ was used to calculate the magnetic exchange coupling constant (*J*) involving the two metal ions in **V₂**.

Results

The calculated vibrational spectra (IR and Raman) show good correlation with the experimentally recorded one, corroborating with the optimization geometry. The optimized structure of **V₂** shows that the vanadyl group and the bis-bidentate oxalate bridge lies in an equatorial plan with the two V=O groups occupying trans positions, while the terminal oxalate and the water ligands are positioned perpendicular to this plane (Fig. 1a). Bader's charges for the vanadium atoms of +2.547 a.u. agree with the lowering of the formal value of 4+ due to charge donation from the ligands to the metal centers. The potential magnetic exchange coupling involving the metal ions of the $\{VO(\mu-ox)VO\}^{2+}$ core was investigated. The resulting value of *J* = -3.61 cm⁻¹ is consistent with a weak antiferromagnetic exchange propagated between the two vanadium(IV) ions (*S* = ½). This result agrees with the experimental χ_{MT} value of 0.698 emu K mol⁻¹ determined for powdered **V₂** at 297 K.

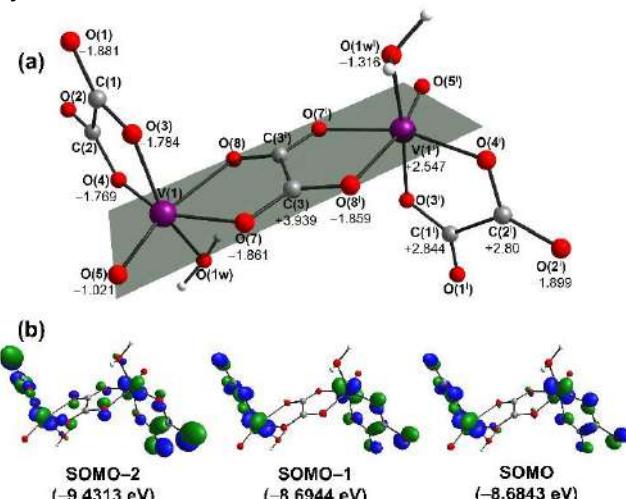


Figure 1. (a) Optimized geometry of the binuclear anion in **V₂** showing the Bader charges, and (b) graphic representation of frontier molecular orbitals of **V₂**.

The frontier orbitals of **V₂** (Fig. 1b) show that both vanadium centers and terminal oxalate ligands contribute significantly to the SOMO and SOMO-1, while the bridging oxalate participates in the composition of the SOMO-2. The calculated electronic spectrum presents three d-d bands at 753, 638 and 502 nm, attributed mainly to $d_{xy} \rightarrow (d_{xz}, d_{yz})$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{z^2}$ transitions. Those three transitions are present in the experimental spectrum as a broad band and reinforce the distorted octahedral geometry of a vanadyl(IV) complex.

Conclusions

The combination of the ω B97XD functional and the def2TZVP basis set was used to calculate the optimized geometry of **V₂**, and the resulting theoretical IR, Raman and Uv/Vis spectra are in good agreement with those obtained experimentally. The Broken-Symmetry approach proves to be a useful tool to determine magnetic properties, and the methodology utilized in this work could be applied to other vanadium complexes.

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ESTUDO DFT DAS PROPRIEDADES ESTRUTURAIS E TERMOQUÍMICAS EM COMPLEXOS DE BISMUTO COM LIGANTES MESOIÔNICOS

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Palavras-Chave: complexos de bismuto, ligantes mesoiônicos, DFT.

INTRODUÇÃO

Complexos de bismuto com ligantes de enxofre doadores são promissores agentes anticâncer¹. Tem-se observado que ligantes mesoiônicos com o anel 1,3,4-tiadiazólio apresentam diversas propriedades farmacológicas³. Este trabalho pioneiro tem como objetivo realizar o estudo teórico a nível DFT das propriedades geométricas e termodinâmicas dos complexos $[BiX_3(L)]$ Onde X= F, Cl ou Br; L= 4,5-difenil-1,3,4-tiadiazólio-2-tiolato (M1), 4-fenil-5-(4-clorofenil)-1,3,4-tiadiazólio-2-tiolato (M2) e 4-fenil-5-(4-metilfenil)-1,3,4-tiadiazólio-2-tiolato (M3), com a finalidade de avaliar a estabilidade dos complexos.

METODOLOGIA

Uma busca conformacional da interação do $BiCl_3$ com o ligante M1 foi realizada considerando os modos de coordenação mono e bidentado por meio dos átomos de S e N do mesoiônico, Figura 1.

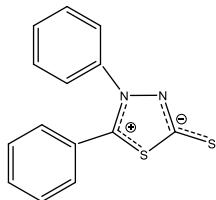


Figura 1. Estrutura do ligante mesoiônico M1.

As geometrias dos complexos foram otimizadas e suas frequências vibracionais calculadas a nível M06-2X/def2-TZVP com potencial efetivo do caroço para Bi. A partir do confórmero mais estável do complexo $BiCl_3M1$, foram construídas e otimizadas as estruturas dos demais complexos. Os parâmetros termodinâmicos para a reação de complexação em fase gasosa e em metanol com modelo de solvente implícito (SMD) foram calculados. Todos os cálculos foram realizados no programa Gaussian 09.

RESULTADOS

A Figura 2 mostra as estruturas otimizadas dos 4 confórmeros e na Tabela 1 as suas energias relativas. No confórmero mais estável (**a**) o Bi se coordena por meio do átomo de nitrogênio com o

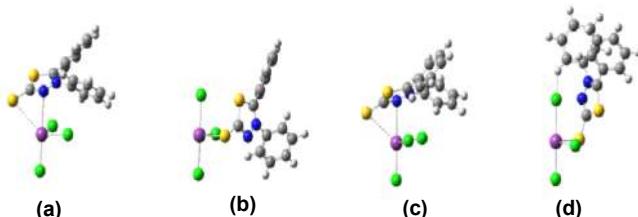


Figura 2. Estruturas otimizadas dos confórmeros em fase gasosa.

ligante na posição axial, e é estabilizado por uma interação fraca Bi-S.

Tabela 1. Energia livre de Gibbs relativa, distância de ligação (Å) e ângulo de ligação (°) dos confórmeros de a-d..

Composto	$\Delta G(kJ.mol^{-1})$	Bi-S	Bi-N	N-Bi-S
a	0,00	3,34	2,88	50,28
b	37,00	2,65	4,00	41,40
c	0,01	3,34	2,88	50,28
d	16,57	2,62	4,06	40,77

Na Tabela 2, são mostrados os parâmetros termodinâmicos para a reação de complexação em fase gasosa e em metanol. Os dados mostram que todas as reações em fase gasosa ocorrem espontaneamente. Em solução, porém apenas a formação dos complexos BiF_3M2 e BiF_3M3 não é espontânea.

Tabela 2. Parâmetros termodinâmicos da reação de complexação.

Complexos	Gás (kJ.mol ⁻¹)			Metanol (kJ.mol ⁻¹)		
	ΔG	ΔH	$T\Delta S$	ΔG	ΔH	$T\Delta S$
$BiCl_3M1$	-48,20	-99,87	-51,67	-10,91	-55,82	-44,90
$BiCl_3M2$	-49,28	-99,36	-50,08	-4,36	-52,92	-48,57
$BiBr_3M1$	-50,49	-101,08	-50,59	-16,28	-61,94	-45,66
$BiBr_3M2$	-49,31	-100,27	-50,96	-12,57	-59,10	-46,53
$BiBr_3M3$	-51,53	-101,48	-49,96	-17,00	-60,88	-43,88
$BiFl_3M1$	-51,14	-99,37	-48,23	-6,23	-47,10	-40,87
$BiFl_3M2$	-49,91	-98,54	-48,63	4,61	-43,87	-48,48
$BiFl_3M3$	-54,09	-98,66	-44,58	0,60	-46,00	-46,60

CONCLUSÃO

A partir da geometria mais estável dos complexos os valores de ΔG e ΔH de reação são todos negativos em fase gasosa e em solução, indicando um processo termodinamicamente favorável, exceto para a reação de formação do BiF_3M2 e BiF_3M3 em solução.

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Revisited INDO/1 parametrization of resonance integrals for Hydrogen

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Keywords: semiempirical, INDO/1, rotovibrational spectroscopy

Introduction

In this work we revisit our parametrization [1] of the semiempirical INDO/1 method. It is well known from the effective Hamiltonian theory of Freed [2] that a semiempirical valence shell Hamiltonian should reproduce the exact spectroscopic results. Most semiempirical methods have chosen to obtain the parameters through extensive statistical sampling of the parameter hypersurface. Since the only representative molecule (for practical purposes) containing *only* hydrogen is H₂, we have opted to study the hypersurface using it as a probe. The aim here is to verify if we can reproduce a set of five rotational, eight vibrational and three thermochemical properties using only three semiempirical parameters (namely m , α and β as in our previous paper [1]).

Methodology

All quantum chemical INDO calculations were carried out using an old copy of the BIGSPEC code running under Ubuntu operational system in a personal computer. The calculated potential energy surface was then fitted to the familiar Dunham expression [3] by a FORTRAN code written by one of us (JDDMN), returning the full set of spectroscopic constants.

Results

Our final set of bonding parameters is $m = -0.36812$, $\alpha = -0.070106$ bohr⁻² and $\beta = -10.7482$ eV. Table 1 shows the calculated properties obtained with this set. All the rotational and vibrational spectroscopic constants are very close to the values obtained by Fink, Wiggins and Rank [4]. Vibrational overtones appear to deteriorate for higher vibrational states. This is most likely associated with the well-known fact that the Dunham expansion is valid only at the bottom of the well, probably in the lowest three or four vibrational levels. On the other hand, the calculated dissociation energy exhibits a larger error (about 1730 cm⁻¹ relative to the very accurate value of Cheng and coworkers [5]) because we have estimated it by using the familiar Birge-Sponer approximation,

$$\omega_e \chi_e = \frac{\omega_e^2}{4D_e} \Rightarrow D_e = \frac{\omega_e^2}{4\omega_e \chi_e}$$

which is exact only for the Morse potential.

We have also compared the few first lines of the calculated Raman spectrum to the line list published by Campargue and coworkers [6]. Similarly to the vibrational overtones, there seems to be a slight deterioration of the results for larger values of J .

Table 1. Summary of INDO/1 results for H₂.

	This work	Observed	Ref.
Rotational			
R_e (Å)	0.74017	0.74144	8
$B_e \approx Y_{01}$ (cm ⁻¹)	61.074	60.859	4
$D_e \approx Y_{02}$ (cm ⁻¹)	-0.04709	-0.04710	4
$H_e \approx Y_{03}$ (cm ⁻¹)	5.45×10 ⁻⁵	4.9×10 ⁻⁵	4
$\alpha_e \approx -Y_{11'}$ (cm ⁻¹)	3.0412	3.0622	4
Vibrational			
$\omega_e \approx Y_{10}$ (cm ⁻¹)	4401.223	4401.217	4
$\omega_e \chi_e \approx -Y_{20}$ (cm ⁻¹)	121.343	121.336	4
$\omega_e \chi_e \approx Y_{30}$ (cm ⁻¹)	-0.094	0.812	4
$\omega_e \chi_e \approx -Y_{40}$ (cm ⁻¹)	0.089	0.050	4
$\Delta G(0-1)$ (cm ⁻¹)	4157.786	4161.166	6
$\Delta G(0-2)$ (cm ⁻¹)	8069.455	8087.006	6
$\Delta G(0-3)$ (cm ⁻¹)	11730.16	11782.39	6
$\Delta G(0-4)$ (cm ⁻¹)	15132.93	15250.37	6
Thermochemistry			
Y_{00} (cm ⁻¹)	8.66	8.90	7
zpe (cm ⁻¹)	2178.9	2179.3	7
D_e (cm ⁻¹)	39909.1	38178.9	5
Rotational Raman			
S(0)	358.98	354.37	6
S(1)	602.11	587.03	6
S(2)	851.09	814.42	6

The accuracy holds for all six isotopologues of H₂.

Conclusions

The current set of semiempirical INDO/1 parameters for hydrogen allows us to (very) accurately reproduce experimental results of a large set of molecular properties. We now intend to verify if this treatment can be extended to other main group elements (Li-F).

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Topography of the Free Energy Landscape on the Claisen-Schmidt Condensation: Solvent and Temperature Effect in the Rate-Controlling Step

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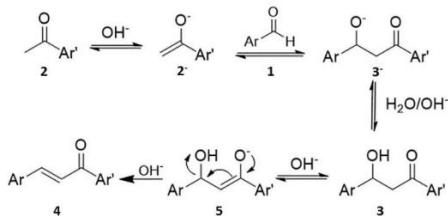
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Palavras-Chave: Chalcone, Free energy landscape

Perrin and Chang's study¹ has found that hydroxide elimination and the C=C bond formation step in base-promoted aldol condensation have a strong influence on the overall rate of the reaction, in contrast to the well-accepted first enolization or C–C bond formation step (see Scheme 1).



Scheme 1. General Formation of base-catalyzed chalcone 4 from benzaldehyde 1 and an acetophenone 2: (R1) first enolization, (R2) C–C bond formation, (R3) proton equilibration, (R4) second enolization, and (R5) hydroxide elimination and C=C bond formation

In a recent paper² we applied theoretical models to the prototypical reaction of chalcone formation and the complete free energy profile of the Claisen-Schmidt condensation was assessed, revealing how the protic solvent and a slight increase in temperature can affect the rate-controlling step.

Stationary points of the elementary steps were optimized employing the compound model B2PLYPD/AUG-ccpVDZ//B3LYP/6-31+G(3df,3dp) level of calculation which SMD solvation and Grimme's dispersion corrections was applied for both water and acetonitrile environment. Additional calculation was performed using explicit-implicit hybrid treatment using the same level of theory.

The reaction rate constants for all five steps over the experimental temperature range (273 – 373 K) were calculated using conventional Transition-State Theory including Skodje-Truhlar quantum tunneling corrections. To account for dynamical effects of the solvent in the elementary steps, Kramers transmission was added to reaction rate constants allowing for a more realistic description of the continuum solvation model.

Figure 1 shows the complete free energy profile of Claisen–Schmidt, revealing how a protic solvent can induce the second enolization as the rate-controlling step (RCS).

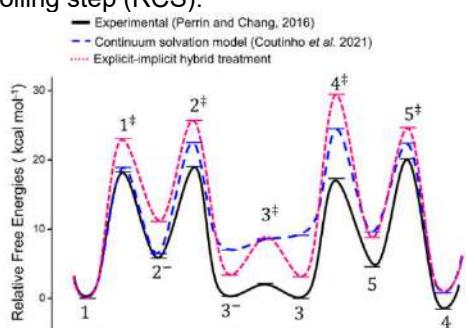


Fig. 1. Gibbs Free Energy for title reaction estimated experimentally by Ref.[1] (black solid line), calculated in continuum solvation medium (dashed blue line) and in explicit-implicit hybrid treatment (dashed pink line).

In Summary, our rate constant calculations corroborated the Chang-Perrin's conclusion supporting the faster reversion from ketol 3 to the reactants 1 and 2 when compared with progression to 4. However, we expanded the comprehension of the solvent and temperature effect on the selection of R4 or R5 as RCS for chalcone formation: increase of temperature and the presence of protic solvent induce R4 as RCS.

Furthermore, the hypothesis that the overall inverse kinetic isotopic effect eliminated R4 as RCS should be carefully evaluated since our results demonstrated that step R2 also supplies this limiting condition. The mechanism of the Claisen-Schmidt condensation can be strongly affected by different physicochemical conditions provoking substantial changes in the Gibbs Free energy profile of steps R1 to R5.

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MULTI-REACTIONAL MULTICONFORMATIONAL KINETIC STUDY OF ETHIL VINYL ETHER (EVE) + OH REACTION

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Keywords: Canonical Variational Transition State Theory, Density Functional Theory, EVE + OH

Introduction. Aliphatic ethers have been suggested as fuel additive, with potential to reformulate the energetic matrix. Molecules in this class are relevant both in Atmospheric and Combustion Chemistry, and learning about its reactivity is important to elucidate its behavior and modulate a precise reactional mechanism.¹ The combustion mechanism starts by unimolecular steps and bimolecular reactions with OH radicals, following hydrogen abstraction and OH addition channels.² In a similar way, at atmospheric conditions, OH radicals are the main precursors of oxidation process of these ethers.³ This study focuses on the EVE + OH reaction, aiming at describing the kinetics of addition and hydrogen abstraction channels.

Computational Methods. Theoretical calculations have been performed at the M06-2x level with the aug-cc-pVTZ basis utilizing the ORCA software. In comparison with the literature, this work brings a more detailed picture of the VEE+OH reaction. Rate coefficients were calculated in a large temperature range, including typical atmospheric and combustion conditions.

Results and Discussion. The conformational analysis and Boltzmann populations suggested that 4 conformations are relevant to the global kinetic reaction. Therefore, the corresponding intermediates and saddle points have been located. Similarities of extreme importance have been revealed important to the prediction of the reaction mechanism. The connection between the specific conformer and its intermediate and saddle point was confirmed by Intrinsic Reaction Coordinate (IRC) and Scan calculations, which allowed the proposal of new reaction channels with multiple possibilities, therefore a multiconformational multireactional study. The complete reaction mechanism including all conformations was proposed, and the relative energy values includes vibrational zero-point energy correction were calculated. Relative energies obtained for saddle points and intermediates are -3.93, -2.14, -1.67 kcal mol⁻¹ (addition channels) and 1.09, 3.00, 3.58, 4.30, 4.86 kcal mol⁻¹ (hydrogen abstraction channels) and -4.13 kcal mol⁻¹ to intermediates. The energies calculated by Han and coworkers⁴ overestimate ours. Rate coefficients were calculated in a vast temperature range of 200 – 2500 K, using the home-made kinpro package,⁵ being the

Canonical Variational Transition State Theory (K^{CVT}) adopted to calculate reagents to intermediates paths and Conventional Transition State Theory (K^{TST}) for intermediate, passing by saddle points to products path. Corrections for the Morse Oscillator and Wigner Tunneling were included in the rate coefficients. In a first glance, the qualitative behavior was maintained as shown in the scarce literature of theoretical calculations⁴ – addition channels dominating the global reaction within a temperature range from 200 to 400 K.

Partial Conclusions. The quantitative analysis still needs to match experimental global rate coefficient calculations data, showing rate coefficients estimated as $7,00 \times 10^{11}$ cm³ molecule⁻¹ s⁻¹ at 298 K.^{6,7} Qualitative behavior of global kinetics domination by addition channels were shown within our mechanism formulation. Nevertheless, the proposal of a precise kinetics of VEE + OH global reaction will be acquainted.

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Accurate determination of relative stability and sublimation temperatures of α -, β - and γ -glycine polymorphs

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Palavras-Chave: phase transition, sublimation, polymorphism.

Introduction. Experimental thermodynamic data related to solid phase transitions are limited, encouraging the development and assessment of theoretical models. Glycine is the simplest amino acid and shows three different stable polymorphs at ambient conditions: α -, β - and γ -glycine. Experimental heat capacity measurements suggested the stability ranking of the crystalline phases as $\gamma > \alpha > \beta$.^[1] Fundamental experimental thermodynamic data for the crystalline phases and solid-vapor equilibrium (SVE) are available for glycine, although they are limited to narrow pressure and temperature ranges. This work introduces a detailed evaluation of the solid-solid and solid-vapor equilibria. The predicted values are evaluated by comparison with experimental and previously reported theoretical data.

Computational details. Periodic calculations for the crystalline phase were performed at the PBE-D3 level. Ultrasoft pseudopotentials (USPP) and a kinetic cutoff energy of 80 Ry were adopted. Phonon frequencies were obtained by means of phonon DOS calculations (DFPT formalism). Thermodynamic properties for the crystalline phases were obtained adopting the quasi-harmonic approximation and Vinet equation of state. Gas-phase thermodynamic data were evaluated at the PBE/6-311+G(3df,2p) level. Cohesive energies were evaluated by careful assessment of the lattice energy, proton transfer energy and conformational relaxation terms, calculated at the CCSD(T)/CBS level. Sublimation properties were evaluated by means of the Clausius-Clapeyron equation at the reference point in which $\Delta G_{\text{sub}} = G_{\text{gas}} - G_{\text{crystal}} = 0$, at 1 Pa.

Results. Gibbs free-energy calculations (**Figure 1**) suggested a phase transition between the γ - and α -crystalline phases at 446.86 K,^[2] in excellent agreement with the experimental report, 440 K.^[1] Moreover, correct stability of glycine polymorphs ($\gamma > \alpha > \beta$) was obtained. Entropy values for each crystalline phase showed absolute deviations of -5.27, 0.13 and -5.42 J mol⁻¹ K⁻¹ for α -, β - and γ -glycine, respectively. Transition enthalpy was obtained as $\Delta H_{\gamma \rightarrow \alpha} = 0.2$ kJ mol⁻¹, at 446.86 K. Remarkable agreement between predicted and experimental^[3] sublimation temperatures was achieved, as shown in **Figure 2**. Sublimation enthalpy was determined as 125.71 kJ mol⁻¹. Errors in the calculated sublimation temperature values are of -5.31 K, at 0.1 Pa, and -3.80 K, at 1 Pa, much lower than the typical

errors in theoretical predictions.^[4] This agreement was achieved mainly due to (i) adoption of a scaling factor for the vibrational frequencies for crystalline and vapor phases and (ii) high-level treatment of gas-phase transformations (CCSD(T)/CBS).

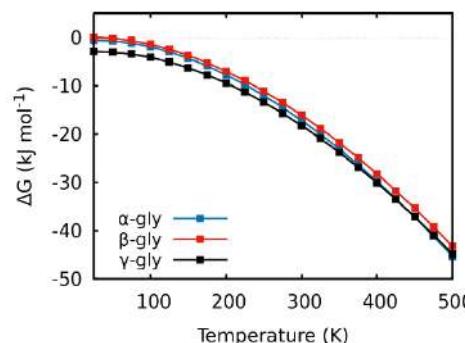


Figure 1. Gibbs free-energy as a function of T, at 1 bar.^[2]

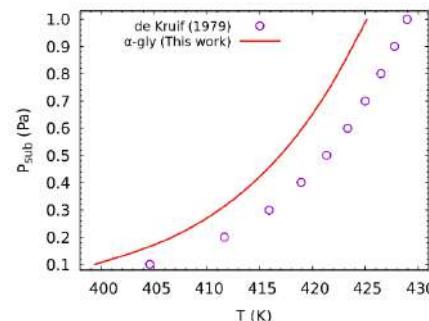


Figure 2. Predicted and Experimental^[3] SVE data.

Conclusions. Relative stability and phase transition thermodynamic data for glycine polymorphs and solid-vapor equilibrium were obtained in excellent agreement with experimental data. Finally, these computational procedures can be extended to other molecular crystals, in order to introduce relevant and accurate thermodynamic data for solid-solid and solid-vapor equilibria, which still lack in the literature.

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Analysis of chemical bonds in S_N2@C and @Si reactions mechanisms in the gas phase

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Keywords: QTAIM, overlap model, Local Vibrational Modes, S_N2 reactions.

Introduction

Understanding the key aspects of chemical reaction mechanisms is usually focused on the profile energetic surface (PES) energetic and structural. However, bond analysis methodologies can add information about the reaction mechanisms. An attractive reaction to apply bond analysis methods is the bimolecular nucleophilic substitution (S_N2). A peculiar feature of this reaction in the gas phase is the PES dependence on the atomic center and/or substituent group nature¹ (Figure 1), generally attributed to steric effects. The central key of this work is to apply the QTAIM², overlap properties³ (OP), and Local vibrational mode (LVM) theory⁴ models to study the chemical bonds (broken, formed, and spectator) in stationary points of the Cl⁻ + XR₃Cl S_N2 reactions, with X=C, Si, and R=H, F, Cl, Me, and Et.

Methodology

The optimized geometries and frequencies were calculated using the ω -B97X-D and OLYP functionals, and SPK-TZP basis set using GAMESS and Gaussian16 programs. The QTAIM, OP, and LVM descriptors were calculated with the Multiwfn, ChemBOS, and LmodeA software, respectively.

Results and discussion

For the S_N2@C reactions, the reactants and products are separated by a pentacoordinate transition state (TS) structure, corresponding to a saddle point in the PES, as can be seen in Figure 1. On the other hand, for S_N2@Si reactions, a stable pentacoordinate transition complex (TC) is observed.

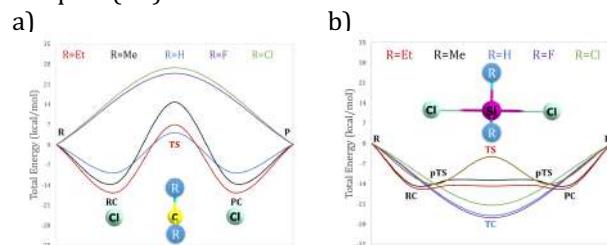


Figure 1. PES obtained for the Cl⁻ + XR₃Cl S_N2 reactions, where X = C, Si, and R = H, F, Cl, Me, and Et. R = reactants, RC = reactant complex, TS = transition state, TC = transition complex, PC = product complex, and P = products.

The chemical bond descriptors $\nabla^2 \rho_{BCP}$ and H_{BCP} for the studied systems are depicted in Figure 2a, while overlap properties and LVM force constants k_n^a are shown in Figures 2b and 2c. In Figure 2a, the empty circles and lozenges represent C-R and Si-R bonds in CR₃Cl and SiR₃Cl respectively, while filled circles and lozenges represent the Cl⁻-(C, Si)R₃Cl complex. Using the Cremer-Kraka Criterion, C-R bonds (empty circles)

are indicated to be more covalent, presenting more negative H_{BCP} and $\nabla^2 \rho_{BCP}$ values, compared with Si-R bonds (empty lozenges).

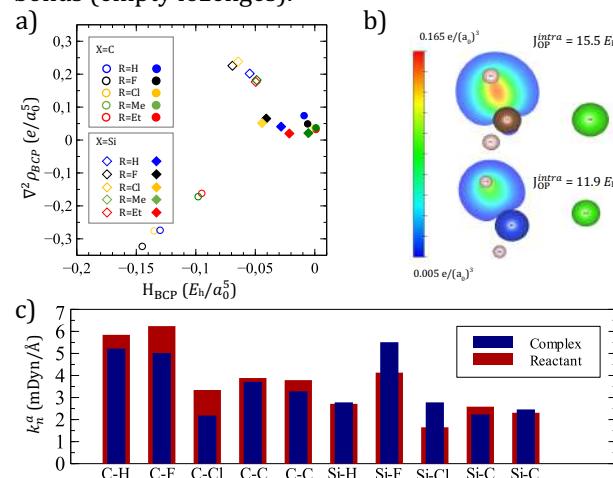


Figure 2. QTAIM descriptors of the spectator chemical bonds (X-R) in XR₃Cl and Cl⁻···XR₃···Cl, (X=C, Si) (a); Overlap density map and repulsion energies for C-H in CH₃Cl and Si-H in SiH₃Cl (b); and local force constants k_n^a for spectator chemical bonds (X-R) in X(R)₃Cl, (X=C, Si) (c).

Following this trend, the overlap properties point to C-R bonds with greater density concentration than Si-R bonds, as represented in overlap density maps in Figure 2b. Also, the overlap Coulomb repulsion energy (J_{OP}^{intra}) is generally greater in C-R than in Si-R in XR₃Cl systems. These results indicate that the steric hindrance experienced by Cl⁻ in S_N2@C reactions is probably associated with the greater covalent nature of C-R bonds, that concentrate density along the chemical bond more efficiently than in Si-R. Additionally, the LVM analysis reveals stronger C-R bonds (with greater k_n^a values) than Si-R ones. This result also agrees with the TS behavior of S_N2@C reactions, in which bonds hamper the S_N2 attack more efficiently.

Conclusion

Chemical bond descriptors (QTAIM, OP, and LVM) indicate significant changes in the properties of the spectator bonds along the PES in the S_N2 reactions.

Acknowledgments

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Determinação de constantes espectroscópicas precisas para o sistema Li₂ via Monte Carlo Quântico

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Palavras-Chave: Monte carlo quântico, PECs, Constantes espectroscópicas.

Introdução

O método monte carlo quântico de difusão (DMC)¹ é um método estocástico e é reconhecido pela grande eficiência em determinar propriedades energéticas. Devido a tal característica, resolveu-se construir curvas de energia potencial (PECs) via DMC. A avaliação da qualidade dos resultados obtidos pelo monte carlo foi feita a partir da determinação de propriedades espectroscópicas por meio do método da Representação da Variável Discreta (DVR).² Utilizou-se para o estudo, o sistema Li₂.

Metodologia

A construção da PEC foi feita através do método DMC. A função de onda teste utilizada foi uma função multideterminante, derivada do método MCSCF. Utilizou-se ainda os determinantes derivados do método CI para a construção da função final para o DMC. Trabalhou-se também com a correlação eletrônica de forma explícita por meio da utilização do fator Jastrow. Utilizou-se o pacote computacional GAMESS para a geração da função de onda teste e o CASINO para os cálculos DMC. Os ajustes das curvas de energia potencial foram feitos por meio da fórmula analítica *Bond Order* com 11 coeficientes. Já as propriedades espectroscópicas foram obtidas por meio do método DVR, em que se destacam as constantes espectroscópicas harmônica (ω_e), anarmônica (ω_{ex_e} , ω_{ey_e}) e de acoplamento rovibracional (γ_e e α_e). Determinou-se também a constante rotacional de equilíbrio (B_e).

Resultados

Por meio da metodologia descrita, determinou-se as constantes espectroscópicas rovibracionais que estão presentes na Tabela 1. Observa-se um ótimo resultado comparativo em relação aos valores experimentais (EXP).³ Da mesma forma, pela Figura 1, nota-se que os resultados obtidos via DMC são bem mais estáveis que os resultados obtidos por outro método de referência da química computacional (CCSD(T)).

Tabela 1: Constantes espectroscópicas via DMC-DVR. Todas os valores estão em cm⁻¹.

	CCSD(T)	DMC	EXP
ω_e	345,75	351,28	351,43
ω_{ex_e}	2,11	2,77	2,595
ω_{ey_e}	-2,88x10 ⁻²	2,27x10 ⁻²	-
α_e	6,11x10 ⁻³	1,36x10 ⁻²	7,04x10 ⁻³
γ_e	-1,04x10 ⁻⁴	6,85x10 ⁻⁴	-
B_e	0,6669	0,6801	0,6726

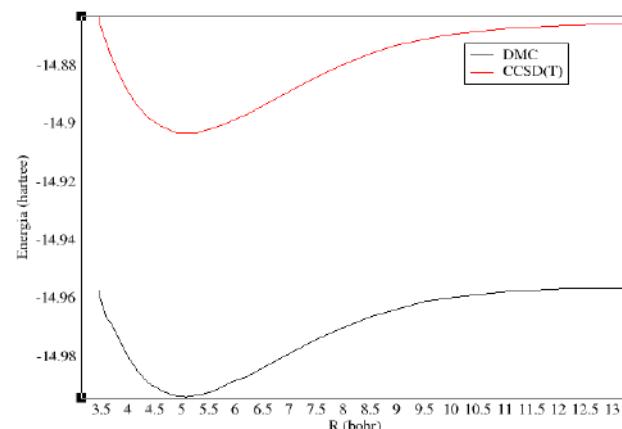


Figura 1: PECs para o sistema Li₂.

Conclusões

A metodologia DMC-DVR foi eficiente em obter resultados para propriedades espectroscópicas em concordância com resultados experimentais da literatura, tendo assim, potencial para se tornar referência na determinação deste tipo de propriedade.

Agradecimentos

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Estudo das propriedades de nanoclusters binários do tipo Pt_nAu_{55-n}

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Palavras-Chave: DFT, clusters, nanoligas

Resumo

Nanoligas a base de platina tem atraído grande interesse nos últimos anos devido às suas propriedades catalíticas e na possibilidade de efeitos sinergéticos em combinação com outros metais de transição, como Au¹. A combinação de metais em sistemas binários, como em clusters, e alterações no tamanho e na distribuição química possibilita mudanças nas propriedades eletrônicas e consequentemente na reatividade química.^{2,3} Dessa forma, é importante compreender as propriedades desses clusters. Para isso, esse estudo tem como objetivo realizar simulações de clusters de 55 átomos de Au-Pt e analisar suas propriedades.

Serão realizados cálculos baseados na teoria do funcional de densidade (DFT), com o funcional PBE. As equações de Kohm-Sham (KS) serão resolvidas usando o método *Projected Augmented Wave* (PAW) com pseudo-potencial implementado no *Vienna ab initio Simulation Package* (VASP). Todas as possíveis composições do tipo Pt_nAu_{55-n} serão exploradas. A busca pelas geometrias de menor energia serão realizadas com o uso de algoritmos genéticos.

Para as diferentes composições de clusters serão determinadas as propriedades como excess energy (E_{exc}), momento magnético total e propriedades estruturais. A E_{exc} mostra a estabilidade relativa de uma nanoliga em comparação com a de um cluster puro contendo o mesmo número de átomos. Essa energia foi calculada utilizando a seguinte equação:

$$E_{exc} = \frac{E_{tot}^{Pt_nAu_{55-n}} - \frac{n}{55} E_{tot}^{Pt_{55}} - \frac{55-n}{55} E_{tot}^{Au_{55}}}{55}$$

Onde $E_{tot}^{Pt_{55}Au_{55-n}}$, $E_{tot}^{Pt_{55}}$ e $E_{tot}^{Au_{55}}$ são as energias totais das nanoligas de Pt_nAu_{55-n}, Pt₅₅ e Au₅₅, respectivamente. Para a análise dos resultados, valores negativos de E_{exc} indicam que a nanoliga é energeticamente favorável e valores positivos indicam que a nanoliga é energeticamente desfavorável.

Em relação às propriedades estruturais, será calculada a distância média das ligações interatômicas no cluster (d_{av}) e a distribuição de átomos de Pt e Au que será determinada por meio do parâmetro de ordem química σ^4 , considerando apenas as ligações mais próximas obtidas através

do effective coordination concept. A equação que define esse parâmetro é:

$$\sigma = \frac{N^{Pt-Pt} + N^{Au-Au} - N^{Pt-Au}}{N^{Pt-Pt} + N^{Au-Au} + N^{Pt-Au}}$$

Sendo N^{A-B} (A, B = Pt, Au) o número total de ligações entre os átomos A e B. Por definição, clusters com $n=0$ ou 55, onde não ocorre ligação entre Pt-Au, ou seja, clusters puros, ordem química $\sigma=+1$. Para clusters binários de Pt-Au completamente homogêneos $\sigma=-1$ e para clusters completamente segregados $\sigma=+1$. Para a compreensão da estrutura eletrônica, será calculado a densidade de estados e o centro de gravidade dos orbitais d (ϵ_d).

Agradecimentos:

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Modelling the adsorption on oxidized carbon nanotubes using a statistical mechanics approach

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Key-words: Carbon nanotube, Adsorption, Multi-layer model

Introduction

Carbon nanotubes (CNT) are widely used to remove pollutants and its oxidization improves the adsorption capacity. The isotherms of adsorption are frequently modelled and interpreted using models like Langmuir and Freudlich. Despite its extensively application, they are predominantly empirical and the adjusted parameters has a lack of physical meaning. [1] An alternative way is to use more advanced models based on statistical mechanics, which provides a better description of the adsorption phenomena and the calculation of thermodynamic properties.[2] In this work, the adsorption mechanism of blue methylene (MB) on oxidized CNT's will be investigated using a statistical mechanics model

Methodology

The statistical mechanics treatment considers that adsorption occurs in a finite multi-layer model (FMLM). The number of adsorbed molecules Q_a can be given as a function of the equilibrium concentration of solution C as [2]

$$Q_a = nN_m \frac{(c/c_1)^n [1 - (N_l + 1) \left(\frac{c}{c_2}\right)^{nN_l} + N_l \left(\frac{c}{c_2}\right)^{n(N_l+1)}]}{\left[1 + \left(\frac{c}{c_2}\right)^n\right] \left[1 - \left(\frac{c}{c_2}\right)^n + \left(\frac{c}{c_1}\right)^n - \left(\frac{c}{c_1}\right)^n \left(\frac{c}{c_2}\right)^{nN_l}\right]}$$

with n the number of molecules for adsorbed site, N_l the number of layers and N_m represents the occupied receptor sites density per surface unit. C_1 and C_2 are related to the energy for the first and the remain layers of adsorption, respectively. All of those are parameters to be fitted in the model.

Results

The equation of FMLM were fitted using the experimental data [3] for the adsorption of MB on pH 7, using as adsorbent an: unmodified CNT (u-CNT); oxidized CNT with debris (fragments of functional groups) removal (@-CNT); oxidized CNT without debris removal (ox-CNT). The adjusted parameters are given on table 1 and the values for the correlation coefficient (R^2) shows that the model fitted satisfactorily the experimental data.

The parameter n shows how the functional groups from oxidization driven the mechanism process. For the adsorption on p-CNT, $n > 1$, therefore the adsorbate molecule binds on a perpendicular orientation suggesting $\pi-\pi$ interactions between the surface and the molecule. On the other hand, the oxidized CNT's shows $n < 1$ resulting on a parallel anchorage, which suggests an electrostatic interaction with the positive charge of MB and the negative charge of functional group presents on CNTs.

Table 1: Fitted parameters of FMLM of adsorption for MB on different CNTs

	u-CNT	@-CNT	ox-CNT
N_m (mg g ⁻¹)	52.3205	56.2899	59.5573
C_1 (mg L ⁻¹)	0.4713	0.0818	0.0045
C_2 (mg L ⁻¹)	11.8855	7.8376	6.8374
N	1.3510	0.8901	0.9126
N_L	2.4099	3.5862	3.5963
Q_{sat} (mg g ⁻¹)	170.3419	178.6714	195.4641
R^2	0.9993	0.9951	0.9933

Conclusions

The FMLM fitted satisfactorily the experimental data of the adsorption of MB on CNT's, providing a better understanding of their mechanism. After this preliminary investigation, the methodology will be carried out in other conditions, such as in acidic and basic solutions. Moreover, the fitted parameters will be used to define the partition function for the system and calculate the thermodynamics properties of the process.

Acknowledgements

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Estudo por docagem molecular da atividade da 2'-hidroxiflavanona na quinase NDK do organismo humano e dos protozoários *Leishmania amazonensis* e *Leishmania major*.

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Palavras-Chave: Leishmaniose, docagem molecular, flavonoide.

INTRODUÇÃO

A leishmaniose é uma doença infecciosa negligenciada, endêmica de regiões rurais, provocada por protozoários do gênero *Leishmania*, que são transmitidos através da picada de mosquitos da subfamília *Phlebotominae*. Os tratamentos atuais insatisfatórios, devido aos efeitos colaterais, por vezes fatais, tornam a busca por novos e alternativos tratamentos necessária para o combate deste mal.

Este trabalho consistiu em analisar, utilizando a técnica de docagem molecular, a interação entre fármacos de referência e substâncias alternativas de origem natural, utilizadas a fim de combater a leishmaniose, tendo como alvo molecular a quinase NDK.

METODOLOGIA

A pesquisa sucedeu-se a partir dos procedimentos mostrados abaixo (Figura 01).

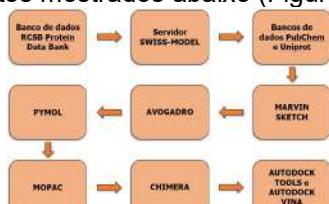


Figura 01: Metodologia aplicada na pesquisa.

RESULTADOS

RESULTADOS
A estrutura tridimensional da NDK foi obtida pelo servidor PDB, código 5GO1 e, através do servidor Swiss-Model (<https://swissmodel.expasy.org/>) foi executada a modelagem comparativa, de modo que os aminoácidos faltantes fossem completados, e a validação do modelo foi feita através do gráfico de Ramachandran onde foi mostrado que 93,8% dos resíduos apresentaram-se em regiões mais favoráveis, (Figura 02).

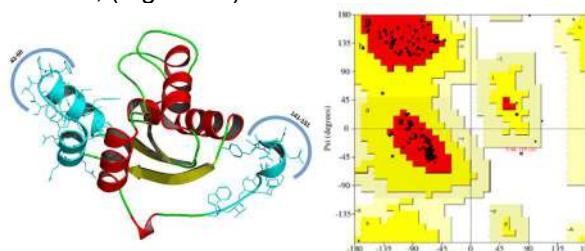


Figura 02: LaNDK completa por modelagem comparativa (esq.) e gráfico Ramachandran (dir.).

As moléculas selecionadas para a pesquisas são mostradas na Figura 03 abaixo:

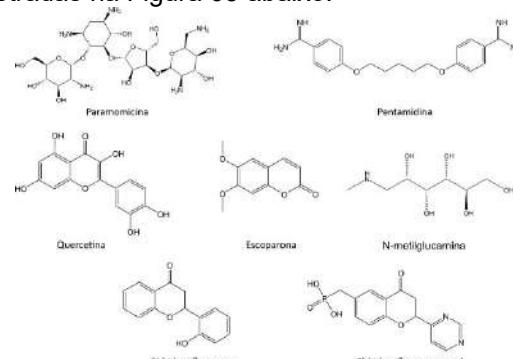


Figura 03: Ligantes selecionados para a pesquisa.

Os resultados de docagem molecular mostraram que as moléculas 2'-hidroxiflavanona, queracetina e pentamidina se ligaram mais fortemente nas enzimas *LaNDK* e *LmNDK* do que na *HssNDK*. Tabela 01.

Ligantes	Valor de energia de docking [kcal/mol]		
	LaNDK	HssNDK	LntNDK
Escoparona	-5,3	-5,3	-5,6
2'-hidroxiflavonana	-6,5	-6,0	-6,7
N-metilglucamina	-5,4	-5,5	-5,8
Paromomicina	-5,9	-6,0	-6,0
Pentamidina	-6,6	-5,7	-6,5
Quercetina	-7,0	-6,6	-7,1
Prostag. O1	-6,5	-7,5	-6,7

Tabela 01: Valores de energia de docking.

CONCLUSÕES

A partir das energias de docagem molecular pôde-se concluir que as moléculas 2'-hidroxiflavonona, queracetina e pentamidina podem ser promissoras para o tratamento da Leshmaniose em humanos, tendo em vista que, competitivamente, pelo fato das energias de docagem molecular serem mais negativas nos protozoários, preferencialmente, irão inibir a NDK dos parasitos e não a humana.

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Correlations between structure and bond dissociation energy of bipyramidal trigonal gallium(III) adducts

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Keywords: DFT, Gallium Adducts, Morse Potential

Introduction

Gallium-coordinated compounds mimic the activity of free radicals in the oxidative stress, inducing apoptosis in several malignant cell lines. These compounds are promising candidates for the development of future anticancer agents.¹ This work evaluated the Ga–L bond dissociation energy (BDE) of bipyramidal trigonal gallium(III) adducts of general formula $\text{GaCl}_3(\text{L})_2$, in which L are the monodentate ligands showed in Fig. 1. The loss of L generates the tetracoordinated GaCl_3L complex. Density Functional Theory (DFT) approach was employed to correlate structural features of adducts with the dissociation energy profiles.

Methods

Six gallium(III) adducts containing O- and N-donor ligands coordinated in the axial positions of $\text{GaCl}_3(\text{L})_2$ were studied (Fig. 1). The DFT calculations were performed using the B3LYP² density functional and the basis set LanL2DZ³ available in the Gaussian16 software.⁴

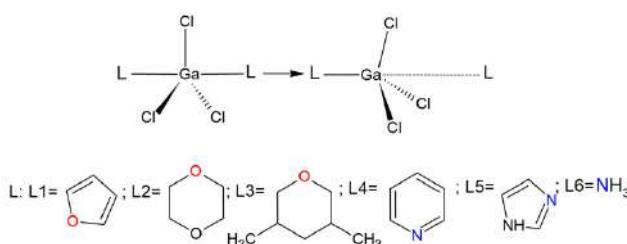


Figure 1. Ligand removal reaction scheme and its structures. The ligand atoms are highlighted in red and blue.

Optimized geometries were calculated without any constraints, followed by relaxed scans optimizations varying the Ga–L bond length. Finally, the energy profiles for the bond dissociation processes were modeled in a Morse-type energy potential curve. Graphs were generated using the Origin 2018⁵ software.

Results

The predicted BDE presented in Fig. 2 reflects the Lewis basicity of ligands and showed that complexes containing O-donor ligands are more prone to suffer dissociation of one ligand when compared with N-donor ones. Moreover, the presence of electronic conjugation in L1 causes a substantial impact on the strength of Ga–O bond, decreasing the estimated value of BDE, when compared with that found for L2.

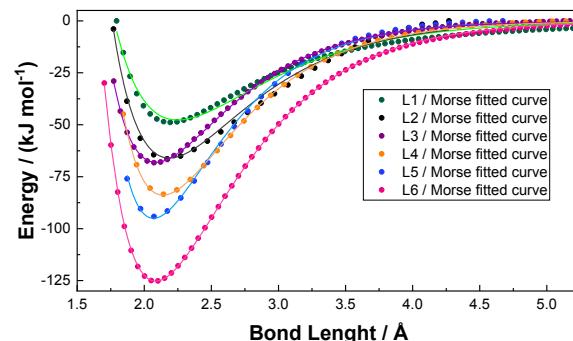


Figure 2. Morse potential fitting for the removal of L from the $\text{GaCl}_3(\text{L})_2$ in which L ligands are shown in Fig. 1.

As shown in Fig. 2, there is a good agreement between calculated data and the Morse-type potential model. Fitted dissociation energies are depicted in Table 1.

Table 1. Fitted dissociation energy for the removal of one of the L ligands in $\text{GaCl}_3(\text{L})_2$

	L1	L2	L3	L4	L5	L6
Energy / kJ mol ⁻¹	48.9	66.4	68.3	83.5	94.2	125

The absolute energy minimum calculated for the Lewis base adduct $\text{GaCl}_3(\text{L})_2$ decreases from L6 to L1, reflecting the availability of the non-bonding electrons of the free ligands. As expected, the highest value was found for L6. The dissociation energy of L2 and L3 points to a low influence of the methyl groups to the basicity of the ligand sites.

Conclusions

The approach using Morse Potential accurately described the energy profile for the dissociation of pentacoordinated Lewis base adducts of gallium (III). The trend observed shows that ligands properties like acidity and delocalization of electronic density influence the BDE. The effect of ligand steric bulk is now under investigation.

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DFT Study of the protonation of a vanadium-dependent haloperoxidase functional model

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Keywords: DFT, Protonation, Vanadium-dependent haloperoxidases

Introduction

Vanadium-dependent haloperoxidases are enzymes that catalyze the oxidation of a halide ($X = Cl^-$, Br^- and I^-) by H_2O_2 to the corresponding hypohalous acids (HOX). Therefore, the HOX reacts with several organic substrates forming a wide variety of halogenated compounds.¹ Most vanadium complexes that act as functional models of these enzymes are active only on acidic media, meaning that the protonation of the catalyst might be an essential step for their activity. In this study, the approach of the H_3O^+ to a compound with the general formula $[VO(bpy)(mal)]$ (in which bpy = 2,2-bipyridine and mal = malate) was studied through Density Functional Theory (DFT). The prototropy between two different protonated forms was studied following a reaction path through a well-defined transition state (TS).

Methods

All calculations were conducted on Gaussian16² employing B3LYP³ as the density functional and LANL2DZ⁴ as the basis set. The molecular geometry of $[VO(bpy)(mal)]$ was optimized to be used as a starting point for the search of transition states (TS) for the protonation step. The TS was then subjected to the Intrinsic Reaction Coordinate (IRC) calculation performed to verify if the reaction path would connect reactants and products generating the energy profile for the protonation and prototropy processes.

Results

The search for a TS for the approach of the H_3O^+ to the vanadyl oxygen of the $[VO(bpy)(mal)]$ led to the structure **C** shown in Figure 1.

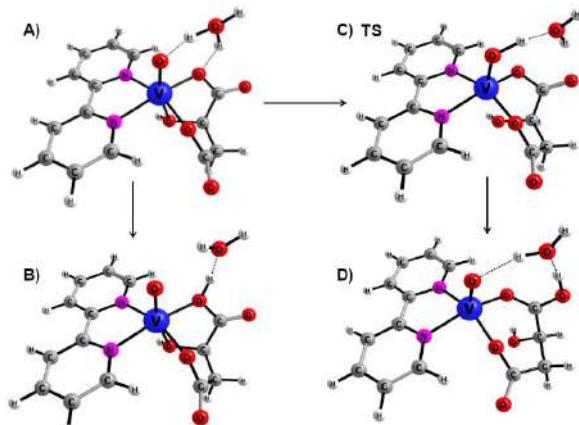


Figure 1. Scheme with the steps involved in the protonation of the $[VO(bpy)(mal)]$.

This result is in line with published results for functional models of haloperoxidases⁵, where no isolated protonated vanadyl moieties were reported. This might be due to their role as transition states or as an unstable intermediate of prototropy processes. The reaction path obtained through the IRC calculation shows that this TS connects the stable species **B** and **D** passing through a molecular structure that is simply the unprotonated $[VO(bpy)(mal)]$ close to the H_3O^+ , as presented in Figure 1 (**C**). The energy profile for the integrated reaction path is shown in Figure 2.

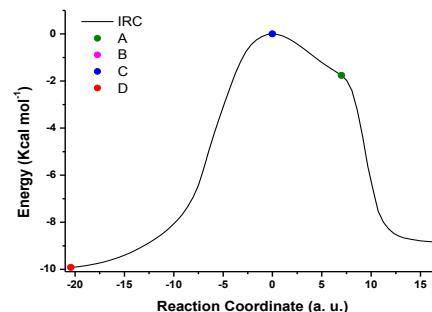


Figure 2. Energy profile for the IRC connecting the three protonated structures of $[VO(bpy)(mal)]$.

As seen in Figure 2, the simple approach of a H_3O^+ leads to system **A** that may produce a stable protonated species **B**, with energy decreasing roughly 7.07 kcal mol⁻¹, or might constitute a reaction transition state with an energy increasing of 1.76 kcal mol⁻¹. The formation of the TS would lead to the most stable protonated species **D** with an energy decrease of 9.92 kcal mol⁻¹. This reasoning implies that the prototropy between the stable molecular species **D** and **B** would have a barrier between 8 and 10 kcal mol⁻¹ and a reaction energy variation of 1.09 kcal mol⁻¹.

Conclusions

There are, at least, two stable protonated species originated from $[VO(bpy)(mal)]$ in acidic medium. These species are linked through a transition state whose energy barrier is between 8 and 10 kcal mol⁻¹.

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Estudo dos Efeitos de Conformação nas Propriedades de Nanoligas de Ouro e Cobre de 55 Átomos

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Palavras-Chave: nanoligas, k-means, DFT.

Os nanoclusters correspondem a uma classe de materiais caracterizados por apresentarem-se na transição entre partículas e sólidos. Por essa característica, os nanoclusters apresentam propriedades fundamentalmente diferentes que a de moléculas ou materiais macroscópicos^[1], o que justifica a ampla gama de estudos presentes sobre essas espécies. Ademais, dentro da classe dos nanoclusters pode-se citar também as nanoligas, das quais propriedades diversas são intimamente dependentes da sua composição, tamanho e conformação em níveis tanto qualitativos quanto quantitativos^[2].

Desta maneira, a versatilidade das nanoligas garante pelo grande número de misturas metálicas possíveis, as quais permitem suas diversas aplicações nas áreas de catálise^[3], biomedicina^[4], equipamentos óticos^[5] e até mesmo como sensores de metais tóxicos^[6]. Dentre os principais candidatos para esses tipos de utilização destacam-se os nanoclusters de ouro por apresentarem estabilidade química na escala nanométrica, baixa toxicidade, caráter ambientalmente amigável e seletividade catalítica preponderada. Com base nisso, o presente trabalho busca investigar os efeitos de dopagem em clusters de ouro com cobre para um total de 55 átomos com o intuito de identificar os efeitos resultantes de conformações e composições diferentes em suas características.

Para a determinação da energia total dos sistemas foram empregados cálculos utilizados o método DFT-D3^[7, 8] juntamente com a aproximação do gradiente generalizado (GGA) proposto por Perdew-Burke-Ernzerhof (PBE) como implementado no pacote de simulação *ab initio* de Vienna (VASP)^[9], empregando os projetores PAW^[10] provenientes do programa. As configurações iniciais dos clusters foram propostas tendo como base geometrias da literatura para sistemas puros de cobre e ouro de 55 átomos. A partir destas, foram geradas outras configurações pela substituição de átomos do sistema por átomos dopantes de cobre, as quais tiveram então suas coordenadas atômicas utilizadas para a construção de suas respectivas matrizes coulombianas (CM) para mapeamento dos potenciais eletrostáticos. Assim, os autovetores das CM foram colocados em ordem decrescente e codificados em vetores para sua aplicação no algoritmo de clusterização *k-means*^[11].

Utilizando as estruturas resultantes do algoritmo, utilizou-se um script em Python para gerar todas as permutações possíveis para os átomos dopantes de cobre. As estruturas permutadas foram então utilizadas para o mesmo procedimento descrito fornecendo as estrutura candidatas finais. Tendo-se finalizado a etapa de seleção das geometrias, os sistemas de Au-Cu resultantes foram otimizados na metodologia de DFT-D3/PBE/PAW.

Nos clusters selecionados, foram calculadas as propriedades como energia de excesso, densidade de estados, comprimentos de ligação médios, raio da estrutura obtido pelo modelo de esferas rígidas (*hard sphere*), número de coordenação efetivo e parâmetro de ordenamento químico. Tais parâmetros foram analisados em conformidade com as frações de átomos de cobre, buscando assim a compreensão dos efeitos da dopagem em conformações tanto superficiais quanto nucleares (*core conformations*) no cluster. Consequentemente, esses resultados levam a informações úteis sobre possíveis mecanismos de formação dessas estruturas.

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Como a Alanina pode ser Sintetizada em Meio Interestelar?

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Palavras-Chave: Aminas, Astroquímica, Moléculas Orgânicas Complexas.

Introdução. Moléculas orgânicas complexas (COM), definidas no contexto da astroquímica como grupos moleculares de seis ou mais átomos incluindo o carbono, têm sido observadas no meio interestelar (ISM). A investigação da reatividade destas espécies neste ambiente nos permite inferir acerca da evolução química das moléculas na Terra primitiva. Acredita-se que várias espécies químicas tenham chegado do espaço à Terra em era prebiótica. Dentre eles, a etilamina ($\text{CH}_3\text{CH}_2\text{NH}_2$) se destaca como um precursor de aminoácidos, como a alanina ($\text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$). Apesar da relevância de COM descobertos no ambiente astroquímico, a falta de parâmetros cinéticos das reações de interesse, permanece um desafio para investigações futuras. Neste trabalho, um mecanismo de reação é proposto para a alanina, visando elucidar os principais caminhos de formação.

Métodos Computacionais. Cálculos teóricos em nível M06-2X/aug-cc-pVTZ foram conduzidos para a localização e caracterização de pontos estacionários. Caminhos de reação foram obtidos por cálculos de coordenada de reação intrínseca. Reações de decomposição da alanina foram calculadas em nível DLPNO-CCSD(T)/def2-TZVPP. Coeficientes de velocidade foram obtidos pelo método variacional canônico, conforme implementado no pacote KINPRO.¹

Resultados. A estratégia de análise retrosintética foi adotada para a investigação do mecanismo de formação da alanina. Partindo desta, a descarboxilação dá origem à etilamina e CO_2 , através de uma barreira de 72,29 kcal/mol, calculados em nível DLPNO-CCSD(T)/def2-TZVPP, tendo uma energia relativa de 0,56 kcal/mol, em relação ao mínimo global. O limite de dissociação da alanina, formando os radicais CH_3CHNH_2 e HOOC , é de 86,47 kcal/mol, sugerindo que a reação de decomposição com barreira é o caminho de reação preferencial de formação de CO_2 . Na continuidade, para investigar os caminhos de decomposição da etilamina, três grupos de reações foram investigados: eliminações de H_2 , dissociações (CC e CN) e dissociações de átomos de hidrogênio. No primeiro grupo, a eliminação dos hidrogênios do carbono central é a de menor barreira (79,81 kcal/mol), formando $\text{CH}_3\text{CNH}_2 + \text{H}_2$. Esta reação compete ainda com a dissociação do radical CH_3 (grupo 2, limite de dissociação 80,38 kcal/mol). As reações do grupo 3,

assim como as demais reações do grupo 1, apresentam barreiras na faixa de 95 – 110 kcal/mol e são desfavorecidas. No entanto, na proposta de formação de etilamina, as reações do grupo 3 mostram-se importantes, já que oferecem os caminhos de recombinação mais exergônicos. Por exemplo, enquanto a decomposição $\text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_2\text{CH}_2\text{NH}_2 + \text{H}$ é proibida pela alta barreira, a etapa reversível, a recombinação $\text{CH}_2\text{CH}_2\text{NH}_2 + \text{H} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2$ mostra-se o caminho mais favorecido, tanto por termodinâmica quanto pela cinética, para a formação de etilamina em meio interestelar. De forma semelhante, a adição de H_2 ao CH_3CNH_2 mostra-se uma etapa com barreira relativamente pequena e, portanto, também possível rota de formação de etilamina. A reatividade do radical CH_3CNH_2 foi também estudada e caminhos que o conectam até as espécies químicas mais simples e mais abundantes no ISM foram propostos. Nossos cálculos sugerem que as etapas $\text{CH}_3\text{CH}_2\text{NH}_2 \leftarrow \text{CH}_3\text{CNH}_2 \leftarrow \text{CH}_3\text{CNH}$ são as mais favorecidas. Além disso, a espécie CH_3CNH pode ser formada a partir das reações $\text{HCN} + \text{CH}_3$, $\text{HNC} + \text{CH}_3$ e $\text{H} + \text{CH}_3\text{CN}$. Todos esses possíveis reagentes são abundantes no ISM. Entretanto, o caminho $\text{CH}_3 + \text{HCN}$ é o mais exergônico (-40 kcal/mol) e o de menor barreira (0,24 kcal/mol), sendo a principal rota de formação de CH_3CNH . Deve-se notar que a recombinação $\text{CH}_3 + \text{HCN}$ leva à CH_3CHN que ainda sofre uma migração de H formando CH_3CNH , com barreira de 29,61 kcal/mol. Porém, essa barreira é menor do que a diferença de energia de formação do CH_3CHN , logo pode ser facilmente ultrapassada.

Conclusões. Dessa forma, conclui-se que a formação de etilamina em fase gás no ISM passa por: $\text{CH}_3 + \text{HCN} \rightarrow \text{CH}_3\text{CHN} \rightarrow \text{CH}_3\text{CNH} \rightarrow \text{CH}_3\text{CNH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$.

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Análise da influência de um modelo de solvatação implícito no estudo do tautomerismo do produto natural 7-*epi*-clusianona

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Palavras-Chave: tautomerismo, RMN, PCM.

Introdução

A elucidação estrutural é uma parte crucial para o estudo das propriedades e atividades biológicas e farmacológicas de moléculas. Assim, determinar a real estrutura de um produto natural se torna uma tarefa altamente necessária. Um dos métodos mais utilizados para o processo de elucidação estrutural é a espectroscopia de Ressonância Magnética Nuclear (RMN). Particularmente, os cálculos teóricos de parâmetros de RMN são capazes de, com baixo custo, auxiliar no processo de caracterização das estruturas de produtos naturais.¹ Neste trabalho, os cálculos de deslocamentos químicos foram utilizados para avaliar a influência de um modelo de solvatação implícito na determinação dos tautômeros mais estáveis da 7-*epi*-clusianona, um produto natural isolado da planta *Rheedia gardneriana*.²

Metodologia

Foi realizada uma busca conformacional utilizando o método Monte Carlo com campo de forças MMFF, no software Spartan'14, para cada um dos 5 diferentes tautômeros possíveis da 7-*epi*-clusianona (figura 1). Os confôrmeros com energia até 10 kcal.mol⁻¹ foram selecionados e, em seguida, foi realizado um cálculo *single-point* de energia, em nível de teoria B3LYP/6-31G(d). A partir dos cálculos *single-point*, foram escolhidos os confôrmeros que obtiveram energia relativa menor que 5 kcal.mol⁻¹ e suas estruturas foram otimizadas em nível de teoria B3LYP/6-31+G(d,p) no software Gaussian'09, em fase gás. Com as estruturas otimizadas, foram selecionados os confôrmeros que apresentavam energia relativa de até 3 kcal.mol⁻¹ e foram realizados cálculos dos tensores de proteção isotrópica em nível de teoria GIAO-B3LYP/6-31G(d), em PCM (benzeno), novamente no software Gaussian'09. Os tensores foram, então, ponderados conforme sua distribuição conformacional, utilizando a equação de Boltzmann. Por fim, os tensores foram transformados em deslocamentos químicos calculados utilizando os valores dos tensores calculados, em mesmo nível de teoria, para o tetrametilsilano (TMS): $\delta_{\text{calc}} = \sigma_{\text{TMS}} - \sigma$.

Resultados

A partir dos valores de deslocamentos químicos de ¹³C e ¹H experimentais, obtidos para os tautômeros B e C,⁴ e calculados para os 5 tautômeros

possíveis, foi realizada a análise estatística DP4+³ obtendo os seguintes resultados (tabela 1):

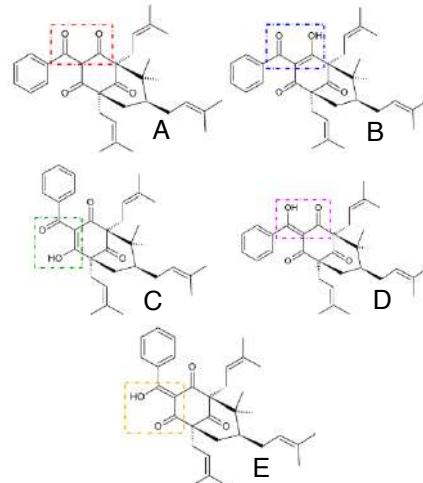


Figura 1: Representações estruturais dos tautômeros da 7-*epi*-clusianona.

Tabela 1: Valores de DP4+³, obtidos a partir dos deslocamentos químicos de ¹³C e ¹H calculados e experimentais.

A	B	C	D	E
Dados experimentais do tautômero B ²				
0,00%	99,99%	0,01%	0,00%	0,00%
Dados experimentais do tautômero C ²				
0,00%	0,00%	100%	0,00%	0,00%

Conclusões

A partir da análise estatística DP4+³, obtida entre os valores de deslocamentos químicos experimentais dos tautômeros B e C,² e os deslocamentos químicos calculados para todos os tautômeros possíveis, foi possível confirmar a presença dos tautômeros B e C em solução de benzeno, como previsto experimentalmente.⁵ Além disso, a aplicação de um modelo de solvatação implícito permitiu a distinção entre os dois tautômeros em solução, ao contrário do obtido em fase gás, apesar da grande similaridade entre os deslocamentos químicos de ambos.

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Development and validation of force field parameters for a vanadium complex from quantum mechanical calculations

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Keywords: *force field, vanadium complex, molecular dynamics.*

Introduction

Cancer therapies based on metal complexes are subjects that receive great attention from the entire scientific community. In this sense, vanadium complexes stand out for being able to modulate autophagic processes¹. Modulation of autophagy by chemical agents can be seen as a new possibility for cancer treatment², in addition to having some advantages compared with chemotherapy. In this context, molecular dynamics (MD) simulations are excellent strategies for designing new drugs. Simulations of this type are highly dependent on force fields (FF). However, it is scarce in the literature of force field parameters for metallic complexes. Therefore, this work aimed to parameterize and validate a new AMBER force field for a vanadium complex (Figure 1) that has proven application in inhibiting autophagy in pancreatic cancer cells¹.

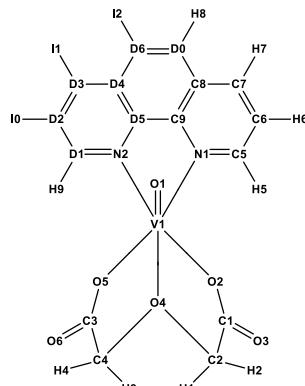


Figure 1 – Vanadium Complex (VC) under study, $[VO(oda)(phen)](H_2O)^{1.5}$.

Computational details

Quantum mechanical calculations were performed using the density functional theory (DFT) level with B3LYP/def2-TZVP for the structure optimization. Furthermore, relativistic effects on VC were investigated using the spin-orbit zeroth order regular approximation (ZORA). Based on the lowest energy spatial arrangement found, the calculation of the RESP charges and the Hessian matrix were performed with the same level of theory. The Lennard-Jones parameters for all atoms, except the vanadium, were assigned according to General AMBER Force Field (GAFF) values. The remaining procedures for the development of FF were

performed using the Paratool plugin, available in the VMD software. Finally, an MD simulation in vacuum was carried out to validate the new force field (New_FF) using the AMBER11 package. The developed parameters were validated by mean VC structural data. Accordingly, the values obtained were compared to some experimental values, acquired by X-ray crystallography³, and a quantum reference (DFT).

Results and Discussion

From Table 1, it is possible to note a good agreement among the values obtained by MD with New_FF, experimental and quantum (DFT) values.

Table 1. Some values of bond lengths (Å) and bond angles (°) obtained by X-ray crystallography (Exp.), quantum mechanics calculations (DFT) and molecular dynamics simulations (New_FF). Standard deviation values in parentheses.

Atom Type	Exp.	DFT	New_FF
V1 – O1	1.59	1.57	1.56 (0.001)
V1 – O5	1.97	1.96	1.91 (0.001)
V1 – N2	2.11	2.18	2.18 (0.001)
N1 – V1 – N2	78.21	75.86	79.26 (0.1)
O5 – V1 – N1	155.92	152.45	153.05 (0.2)
O5 – C3 – O6	124.43	125.84	124.01 (0.1)

Supported by other results obtained by comparing the New_FF and the quantum reference (not shown in Table 1), it is possible to observe relative error values ranging mostly from 0% to 2%. Furthermore, based on RMSD analysis, an oscillation amplitude of 0.6 Å has been obtained.

Conclusion

After the structural validation of VC and the RMSD analysis, it is possible to conclude that a New_FF satisfactorily reproduces the experimental and quantum reference results.

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Ab Initio Investigation of CO₂ Reduction on Stepped Silver Surfaces

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Palavras-Chave: CO₂ electrocatalysis, DFT calculation, Silver stepped surface.

A major problem in modern times is the environmental pollution by gases. Some approaches to decrease pollutants, such as CO₂, have been developed in the past decades. In this context, electrochemical CO₂ reduction reaction (CO₂RR) happens to be an attractive form to approach the problem and is able to convert carbon dioxide into valuable products such as formic acid.

The CO₂RR is known to be efficient over the surface of some transition metals, however it has a slow kinetics, and it competes with the hydrogen evolution reaction (HER). To help in overcoming this issue, in this work we performed a computational study of silver surfaces as potential catalyst. This metal is known to reduce CO₂ to CO with high faradaic efficiency in preference to the HER. The calculations are based on Density Functional Theory (DFT) and with the PBE functional and D3 dispersion correction.

The first part of the research concerns the calculation of converged values for the properties of bulk silver, and also low-miller indexes Ag(100), Ag(110) and Ag(111) slabs. Calculations on the stepped Ag(211) surface were performed with a 3x5x3 slab model, and the surface properties were calculated. Later, we have studied the adsorption of CO₂ reduction intermediates, considering all adsorption sites and possible orientations of the adsorbing molecules. The possibility that single atoms dopants may favor the formation of different products was assessed by substituting transition metal (TM) dopants in the Ag(211) surfaces. This stepped surface has three different spots to substitute an Ag atom with a TM, namely step, terrace and substep. The study is made varying the adsorption sites and these spots.

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Refining Details of the Structural and Electronic Properties of the Copper Site of the pMMO Enzyme from MD and DFT Calculations.

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Palavras-Chave: pMMO, EPR, Molecular Dynamics.

INTRODUCTION

Particulate methane monooxygenase, pMMO, is an integral membrane-bound enzyme that efficiently catalyzes the conversion of methane to methanol under mild conditions. This particulate form of methane monooxygenases enzymes (MMO) found in *methanotrophic* bacteria is the most abundant natural catalyst for methane oxidation, which takes pMMO as a promising base catalytic system for developing new bioinspired catalysts for the selective activation and functionalization of alkanes.^{1,2} In this context, a detailed knowledge concerning the reaction mechanism of pMMO is crucial.

However, there are still open questions about the composition of the active site of this enzyme, since the crystallographic structure was resolved with low resolution (2.68 Å)^{1,2}. For instance, the possibility of that water molecules can coordinate to copper center, since this site is highly solvent-exposed.

A remarkable advance archived in this context was obtained from EPR measurements carried out by Rosenzweig et al, where indeed the results indicated the possibility of water molecules at the first coordination sphere of copper site. Nevertheless, due the complexity of the system we believe that a computational study can contribute to a detailed interpretation of these EPR data.

Thus, in this work we carried out molecular dynamics simulations and DFT calculations to investigate at the molecular level the structural and electronic properties of the active site of pMMO.

METHODS

Coordinates: The initial coordinates of the pMMO model were taken from the crystallographic structure obtained from the PDB (code 3RGB).

MD Simulation: Only the soluble PmoB part was used for the simulation. The membrane and membrane-bound part were not considered. Ensemble NpT ($p = 1\text{ bar}$, $T = 298\text{ K}$), pH 7. Simulation 500 ns. OPLS-AA force field. PBC.

EPR Calculations: To select the structures for EPR calculations, was used the cluster method of Daura, et. al³. With the selected structures, the EPR calculations were performed for 38 structures, using the revPBE, B3LYP and BHANDHYP XC functionals and the Def2-TZVP basis set.

RESULTS

The calculations of EPR parameters of the copper active site of pMMO were performed via a sequential scheme MD/DFT with 38 average structures generated from a cluster analysis with the trajectory of the last 100 ns from the 500 ns MD simulation. A systematic study with different XC functional showed that the best description of EPR parameters is obtained with hybrids functional, with highlights to BHANDHYP. In Fig. 1 is presented the performance of BHANDHYP on the description of hyperfine constant of the copper active site of pMMO enzyme.

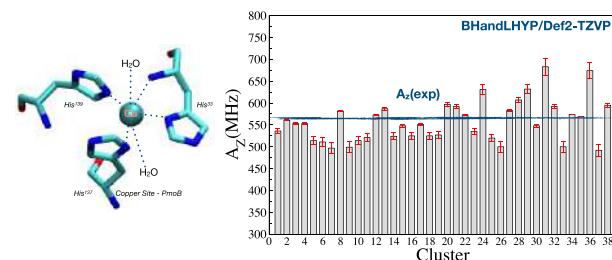


Fig. 1: Hyperfine constant calculated at BHANDHYP/Def2-TZVP level concerning the 38 average structures statistic selected from the last 100 ns of the MD trajectory of the 500 ns simulation.

CONCLUSIONS

The combination of MD and DFT calculations of EPR parameters, and comparisons with experimental EPR data, led to the proposition that the PmoB site is a mononuclear copper complex coordinated by the residues His³³, His¹³⁷, and His¹³⁹ on the equatorial axis and by two water molecules on the axial axis, with one of these water molecules being more labile which may suggest looser coordination to the copper ion, which over time, under the presence of the solvent medium, can alternates between a distorted octahedral and a square pyramidal structures.

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Conductive metal–organic framework based on Zn(II)-porphyrin and C₆₀

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Keywords: MOF, Porphyrin, DFT.

The development of new materials has become a field of interest due to the diversity of applications that they may have. Among these materials, the porous coordination polymers that are formed mainly through ligand-metal bonds to form the so-called “Metal Organic Frameworks” (MOF)¹ stand out. The study of these materials has experienced rapid growth in recent years due to their structural characteristics and properties such as the functionalization of their pores, high specific surface area, low density, and design flexibility, among others². MOFs have been used in photocatalysis³ and adsorption⁴, among other applications⁵. However, its use in electro-conductive applications is limited due to the lack of conductivity in most systems. Porphyrin-based structures doped with fullerene molecules within their pores are attractive candidates as electronic devices due to the increased conductive properties generated by acceptor-donor interactions between porphyrin and fullerene⁶.

In this work, the application of a conductive MOF based on Zn(II)-porphyrin and C₆₀ (Figure 1) as a potential electronic device was evaluated as bulk using density functional theory (DFT) at the theory level PBES and PBE-D3/medium base/pseudopotential pseudodojo and K points 2x2x2. The calculated electronic properties demonstrate a band gap decrease in 0.4 eV of the fullerene-doped MOF (MOFdp) with respect to the undoped MOF, suggesting an important contribution of the acceptor group in the increase of the electron flux in the system. These results are coherent with the density of states calculated that shows an increase in the number of available states close to the Fermi level, for a charge transfer in MOFdp with respect to MOF. The interaction energy, corrected by the counterpoise method, of the fullerene within MOFdp was -0.78 eV, which suggests that the incorporation of fullerene into the system is favorable.

Time-dependent TD-DFT calculations of a MOFdp cluster, performed at the TPSSh/6-31G theory level in the solvent phase, show direct charge transfer bands from porphyrins to fullerene in the near infrared region or also through a visible light excitation photoinduced electron transfer process, demonstrating the influence of fullerene on the increased optical properties of the system.

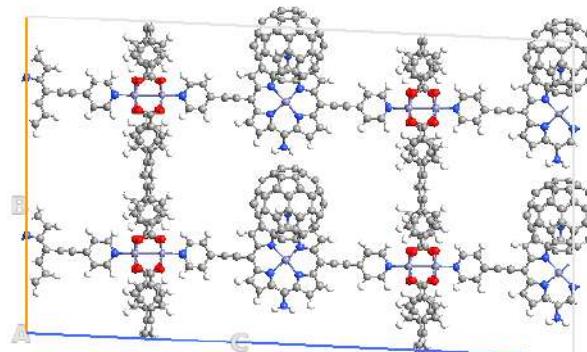


Figure 1. Optimized unit cell of MOFdp (LCAO/PBES/k=2x2x2/pseudodojo)

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XXI SBQT

Estudo da Adsorção de CO₂ em nanoclusters de Cobre dopado com cobalto

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Palavras-Chave: Estrutura eletrônica, DFT, nanoclusters.

Grandes problemas ambientais, como o efeito estufa, são decorrentes do avanço da industrialização e a exploração excessiva dos combustíveis fósseis. São preocupantes os dados atuais sobre o aumento da emissão e alta concentração de gases do efeito estufa, principalmente o dióxido de carbono (CO₂). Diante disso, torna-se necessário encontrar alternativas para novos usos do CO₂, além de soluções para minimizar essas emissões. Uma solução seria convertê-lo em matérias-primas químicas de valor agregado, através do processo de redução eletroquímica, por exemplo [1].

Os catalisadores desempenham um papel fundamental neste processo, uma vez que as etapas de adsorção e ativação do CO₂ sobre superfícies catalíticas são cruciais. Compreender como esses mecanismos acontecem é de extrema importância pois contribui para projetos de sistemas catalíticos mais eficazes.

Recentemente os nanoclusters metálicos têm sido explorados como uma nova possibilidade para a catálise, e eles tem se mostrado bastante eficientes devido às suas propriedades únicas^[2]. Os nanoclusters de Cobre têm recebido atenção especial e são amplamente investigados no processo de eletroredução do CO₂. Estudos mostram que nanopartículas do metal afetam significativamente a termodinâmica da redução do CO₂^[3].

O enfoque deste trabalho é estudar o processo de redução do CO₂ utilizando nanoclusters de cobre dopados com cobalto, do tipo Cu_{55-x}Cox como catalisadores. Foram realizados cálculos em nível DFT, com o funcional PBE^[4], correção de dispersão D3^[5] dentro do método PAW, implementado no pacote VASP.

A síntese dos produtos, comumente hidrocarbonetos, ácido fórmico e álcoois, a partir da redução eletroquímica do CO₂ é uma reação de várias etapas, extremamente complexa e ainda muito pouco elucidada, que inclui a adsorção de diferentes intermediários em sítios ativos de diferentes naturezas químicas^[6]. Serão estudadas as interações entre essas moléculas intermediárias com nanoclusters de Cobre, e será avaliado ainda se o efeito da dopagem com cobalto favorece algum outro produto da eletroredução em específico.

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Estudo de docking molecular e NCI das interações entre a Tacrina, ACh e a acetilcolinesterase humana.

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Palavras-Chave: doença de Alzheimer; docking; NCI; acetilcolinesterase; acetilcolina; tacrina;

INTRODUÇÃO

A doença de Alzheimer (DA), é caracterizada pela perda progressiva das habilidades cognitivas, bem como por mutações no alelo $\epsilon 4$ da proteína imunomoduladora apolipoproteína E (APOE).^[1] São observados nos pacientes a formação de placas senis contendo peptídeos A β , e principalmente, a supressão do neurotransmissor acetilcolina (ACh), a qual é o substrato natural da enzima acetilcolinesterase responsável pela transmissão de impulsos nervosos nas regiões sinápticas.^[2]

A abordagem mais utilizada para o tratamento sintomático da DA é terapia colinérgica, que consiste no uso de fármacos, chamados inibidores de acetilcolinesterase (AChE). Estes atuam de maneira competitiva ou não competitiva com o neurotransmissor e com ação inibitória frente à enzima acetilcolinesterase (AChE).

Estudos de estrutura eletrônica, de docking molecular e análises de interações não-covalentes (NCI) foram empregados para a melhor compreensão das interações entre os ligantes THA e ACh e a enzima acetilcolinesterase humana hAChE visando mapear os aminoácidos envolvidos diretamente no processo de inibição da enzima.

METODOLOGIA

Os estudos de estrutura eletrônica dos ligantes foi realizado usando os métodos B3LYP e MP2, ambos com a função de base aug-cc-PVDZ. O estudo de docking foi feito por meio do pacote AutoDock 4^[3]. A estrutura 3D da proteína hAChE utilizada foi obtida do banco de dados Protein Data Bank (PDB), depositada com código PDB 4BDT.^[5] O espaço de docagem centralizado no resíduo His447 da tríade catalítica, incluindo todos os resíduos do sitio ativo (GORGE). O programa Multiwfn^[4] foi usado para a visualização das isosuperfícies dos estudos de NCI e das respectivas localizações de interações não covalentes.

RESULTADOS

Em relação a ACh e o seu sitio ativo da hAChE, os resultados mostraram que interações do tipo cátion- π e sigma- π são estabelecidas no sitio ativo entre o resíduo Trp86 e a região do nitrogênio quaternário, também foram observadas ligações de hidrogênio e uma interação de atração de cargas com os resíduos Tyr337, Tyr124 e Glu202, respectivamente. Os resultados do estudo de NCI da ACh mostraram contribuições de interações do tipo van der Waals entre o nitrogênio quaternário e os seus respectivos átomos de carbono, como também na região de quebra da molécula para a formação de colina e acetato.^[5]

Os estudos de docking da THA com AChE evidenciaram que a THA é reconhecida no sitio aniónico, periférico e catalítico.^[5] Nesse sentido, notamos interações do tipo π -stacking entre os anéis aromáticos da THA e do resíduo Trp86, além de ligações de hidrogênio com os resíduos Thr86 e Gly82. Em contrapartida a THA em seu estado protonado apresentou um perfil mais coerente com evidências da literatura, com interações no sitio periférico do tipo van der Waals com os resíduos Glu202, Tyr449, Ser203 e Gly121 e no sitio catalítico ligações de hidrogênio com o resíduo His447, relacionadas com o hidrogênio que adicionamos para a formação do ligante. Infere-se a formação da interação clássica do tipo π -stacking sanduíche entre resíduos Trp86 e Tyr337 e a THA (protonada), o qual também foi evidenciado no estudo de NCI, e correspondente ao encontrado na proteína tcAChE, com os resíduos Trp84 e Phe330.^[5]

CONCLUSÕES

Neste trabalho foi observada importância das propriedades eletrônicas e interações moleculares dos respectivos ligantes com os resíduos do sitio ativo, considerando o seu estado de protonação em pH fisiológico. Onde pode ser observado o ancoramento da THA (protonada) dentro do sitio ativo da hAChE, correspondente ao observado experimentalmente nas estruturas cristalográficas.

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CNPq, UnB, PROIC-UnB, LQC.



Avaliação da Cinética de Reações Unimoleculares na Combustão de Dimetoximetano

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Palavras-Chave: coeficientes de velocidade, combustão, éteres de oximetíleno

Introdução. A busca por combustíveis alternativos é importante para a diversificação da matriz energética e geração limpa e sustentável de energia. Nesse sentido, o dimetoximetano (DMM) é um potencial candidato, pertencente ao grupo dos poli(oximetíleno) éteres (OME), que apresentam emissão reduzida de fuligem, CO, NOx e SOx.¹ Investigações experimentais, teóricas e simulações numéricas têm sido conduzidas acerca da combustão e pirólise de DMM. Uma das conclusões mais frequentes é a possibilidade da dissociação da ligação CO ser um canal muito importante para esse consumo aliado às reações bimoleculares. Este estudo busca trazer novas investigações acerca da cinética das reações de DMM.

Métodos Computacionais. Cálculos teóricos foram realizados no nível CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ através do pacote Gaussian, G09, incluindo otimizações das geometrias moleculares, previsão de frequências vibracionais e cálculos de caminhos de reação. Coeficientes de velocidade foram calculados usando o pacote KINPRO.²

Resultados e Discussão. Um esquema detalhado de reações unimoleculares foi proposto para descrever o mecanismo de decomposição térmica de DMM, incluindo dissociações de átomos de hidrogênio e radicais metil e metóxi e decomposições unimoleculares, como mostrado na Figura 1.

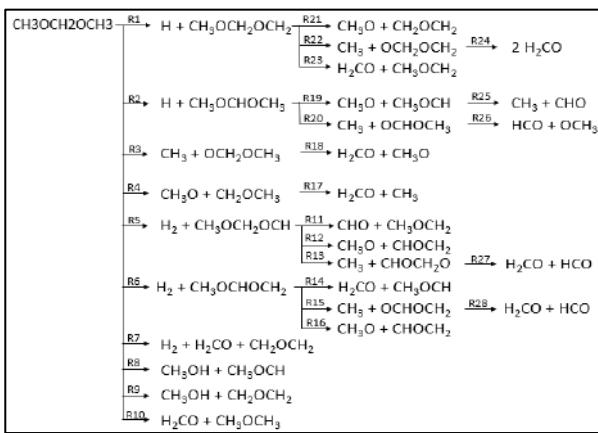


Figura 1: Esquema de reações unimoleculares de DMM.

Dentre as reações investigadas, R3 (DMM → CH₃ + OCH₂OCH₃, limite de dissociação: 80,41 kcal/mol) é o caminho mais favorável, seguido pela dissociação OCH₂OCH₃ → H₂CO + CH₃O (R18, limite de dissociação: 11,75 kcal/mol). Para fins de

comparação, os limites de dissociação de outras dissociações primárias são 85,98 kcal/mol (R4: DMM → CH₃O + CH₂OCH₃), 94,99 kcal/mol (R1: DMM → H + CH₃OCH₂OCH₂) e 97,21 kcal/mol (R2: DMM → H + CH₃OCHOCH₃). R8 foi recentemente proposta e apontada como o mais importante canal unimolecular de DMM.³ Nossos cálculos sugerem que a barreira desta reação é 70,10 kcal/mol (R8a, DMM → CH₃OH + *trans*-CH₃OCH), 72,10 kcal/mol (R8b, DMM → CH₃OH + *cis*-CH₃OCH).

Coeficientes de velocidade foram calculados apenas para as reações unimoleculares mais importantes para o mecanismo (R3, R4, R8), sendo expressos, em s⁻¹, por (energias de ativação são dadas em kcal/mol):

$$K_{R3}(T)=1,8513 \times 10^{15} \times (T^{0,8468}) \times \text{EXP}(-86,26/RT),$$

$$K_{R4}(T)=1,2147 \times 10^{14} \times (T^{0,7559}) \times \text{EXP}(-87,90/RT),$$

$$K_{R8}(T)=3,2990 \times 10^{11} \times (T^{1,0570}) \times \text{EXP}(-70,34/RT)$$

Coeficientes de velocidade variacionais microcanônicos foram também obtidos e serão usados para o cálculo de coeficientes de velocidade dependentes de temperatura e pressão.

Conclusões. R3 é dominante acima de 1000 K, condição típica de combustão em alta temperatura. Abaixo dessa faixa, R8 é o caminho preferencial. Contribuições significativas foram geradas acerca da cinética de decomposição térmica do DMM e OME.

Agradecimentos. O presente trabalho foi realizado com apoio da Coordenação de aperfeiçoamento de Pessoal de Nível superior – Brasil (CAPES)- Código de financiamento 001, FAPERJ, CNPq e da UFRRJ. Os autores também agradecem ao apoio do LNCC (sdumont2019/chamada1/paper194777).

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Estudo Cinético do Mecanismo de Oxidação do Dimetilsulfeto

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Palavras-Chave: Dimetilsulfeto, Reações com radical OH, Dimetilsulfóxido.

Introdução. Desde a publicação de Charlson e colaboradores, em 1987, intensa investigação tem sido conduzida sobre o papel do dimetilsulfeto (DMS) no transporte de enxofre dos oceanos para a atmosfera. O DMS é majoritariamente liberado na atmosfera por espécies de fitoplâncton marinho, e sua oxidação leva à formação de núcleos de condensação de nuvens (CCN), filtrando os raios solares e diminuindo a temperatura na região.¹ A oxidação do DMS é iniciada por radicais OH e descrita por um mecanismo complexo, compostos por inúmeras reações consecutivas, resultando em espécies que contribuem com a acidez de chuvas e formação de CCN.

O objetivo deste trabalho é desenvolver o mecanismo de reação de DMS com OH em fase gasosa que leve até a formação de CCN.

Métodos Computacionais. O estudo foi conduzido utilizando o programa Gaussian09 para cálculos de otimizações de geometrias, frequências vibracionais e caminhos de reação, em nível M06-2X/aug-cc-pVTZ. Cálculos de coeficientes de velocidades variacionais foram realizados, conforme implementação no pacote KINPRO.²

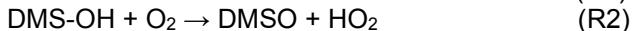
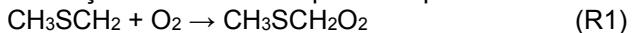
Resultados e Discussão. A oxidação do DMS pelo radical OH pode ser iniciada por caminhos de adição de OH ($\text{DMS} + \text{OH} \rightarrow \text{DMS-OH}$) ou de abstração de hidrogênio ($\text{DMS} + \text{OH} \rightarrow \text{CH}_3\text{SCH}_2 + \text{H}_2\text{O}$). Estas etapas iniciais já foram previamente reportadas.³ Para o caminho de abstração de hidrogênio foi encontrado o coeficiente de velocidade, em 240 K, igual a $2,33 \times 10^{-12} \text{ cm}^3 \cdot \text{molécula}^{-1} \cdot \text{s}^{-1}$. Os coeficientes de velocidade para o caminho de adição do OH ao DMS e sua reação reversa são expressos por (k_f e k_b , em $\text{cm}^3 \cdot \text{molécula}^{-1} \cdot \text{s}^{-1}$ e s^{-1} , respectivamente e energias de ativação dadas em kcal.mol⁻¹):

$$k_f(T) = 3,35 \times 10^{-10} \exp(-0,925/RT)$$

$$k_b(T) = 6,118 \times 10^{15} \exp(-10,679/RT)$$

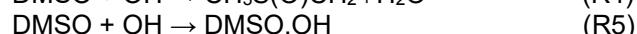
Estes coeficientes de velocidade estão em excelente acordo com o relato de Williams e colaboradores.⁴

As reações entre O_2 e os produtos primários são:



A reação R1 é exotérmica ($\Delta E = -30,98 \text{ kcal.mol}^{-1}$) e apresenta uma barreira de $1,55 \text{ kcal.mol}^{-1}$. Os coeficiente de velocidade (em $\text{cm}^3 \cdot \text{molécula}^{-1} \cdot \text{s}^{-1}$) são expressos por $k(T) = 5,37 \times 10^{14} \exp(-1,9114/RT)$. A reação R2 é um canal de abstração do hidrogênio do produto primário de adição, gerando dimetilsulfóxido (DMSO) e HO_2 , e mostra $\Delta E = -14,80 \text{ kcal.mol}^{-1}$. O ponto de sela foi localizado em nível M06-2X/aug-cc-

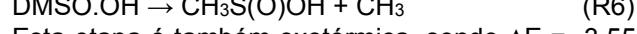
pvdz e deve ainda ser confirmado por cálculos com base de qualidade superior. O canal de adição de O_2 é apresentado na reação R3 formando $(\text{CH}_3)_2\text{S}(\text{O}_2)\text{OH}$ por uma reação endotérmica ($\Delta E = 25,87 \text{ kcal.mol}^{-1}$) sem barreira. Uma vez formado, o DMSO poderá sofre abstração de hidrogênio por reação com OH (R4) ou adição do radical OH (R5).



A reação R4 ($\Delta E = -14,99 \text{ kcal.mol}^{-1}$) mostra uma barreira de $0,80 \text{ kcal.mol}^{-1}$ e coeficientes de velocidade ($\text{cm}^3 \cdot \text{molécula}^{-1} \cdot \text{s}^{-1}$) expressos por $k(T) = 1,85 \times 10^{13} \exp(-0,8551/RT)$. R5 é também um canal exotérmico, sem barreira, com $\Delta E = -10,05 \text{ kcal.mol}^{-1}$ e mostra coeficientes de velocidade ($\text{cm}^3 \cdot \text{molécula}^{-1} \cdot \text{s}^{-1}$) expressos por:

$$k(T) = 4,28 \times 10^{14} \exp(-8,5542/RT)$$

O produto formado nesta etapa sofre dissociação:



Esta etapa é também exotérmica, sendo $\Delta E = -3,55 \text{ kcal.mol}^{-1}$. O ponto de sela para esta reação foi localizado em nível M06-2X/aug-cc-pvdz e ainda necessita de confirmação por cálculos com base de qualidade TZ.

Conclusões. A reação R2 é de grande importância, visto que a rápida formação do DMSO impede a dissociação do aduto DMS.OH, observada na ausência de O_2 . O rápido consumo de DMSO leva a intermediários que poderão formar espécies que contribuem para a acidez de chuvas e formação de núcleos de condensação de nuvens. Portanto, elas formam uma base de reações elementares para a construção do mecanismo detalhado de oxidação de DMS em condições de atmosfera marinha e costeira.

Agradecimentos. O presente trabalho foi realizado com apoio da Coordenação de aperfeiçoamento de Pessoal de Nível superior – Brasil (CAPES)- Código de financiamento 001, FAPERJ, CNPq e da UFRRJ. Os autores também agradecem ao apoio do LNCC (sdumont2019/chamada1/paper194777).

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Theoretical study of the interaction between pure and N-substituted coronene dimers with CO₂

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Keywords: Asphaltene Aggregation, Carbon Dioxide, Environment

INTRODUCTION: Aiming to reduce the impact caused by the emissions of greenhouse gases, mainly carbon dioxide, the oil industry has been looking for mitigation strategies that are capable of capturing and reinjecting the inevitably produced CO₂ in its extraction wells. However, CO₂ interacts with asphaltenes molecules and can promote destabilization, favoring their aggregation and precipitation, which causes serious problems.¹ The precipitation of asphaltenes is directly influenced by changes in the thermodynamic conditions, as well as by the presence of heteroatoms, with the π – π stacking interaction being the main contribution.² The present work aims to evaluate the effect of CO₂ on the stability of the asphaltene aggregation by means of an aromatic model, the coronene (C₂₄H₁₂, Fig. 1a).³

METHODOLOGY: As a first step, a coronene monomer was optimized individually (Fig. 1a). Thereafter, dimeric aggregates were optimized in three different arrangements, privileging stacked approach – Sandwich (SA), Shifted-sandwich (SS) and Crossed (CR) (Fig. 1b, c, d) – starting from the distance of 5.0 Å between the monomers (Fig. 1e).

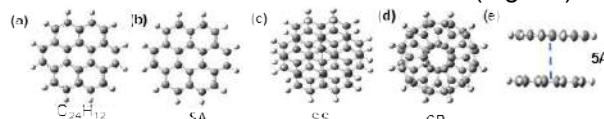


Figure 1. (a) Coronene (C₂₄H₁₂) and pure dimeric aggregates, (b) Sandwich (SA), (c) Shifted-sandwich (SS), (d) Crossed (CR), and (e) initial distance.

Posteriorly, the same systematic was repeated, however, inserting one nitrogen atom in two distinct positions (Fig. 2): central (a) and peripheric (b).

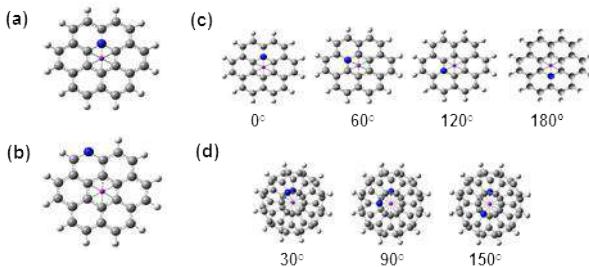


Figure 2. N-substitution in Coronene, (a) central and (b) peripheric, and (c) SA and SS (0°, 60°, 120° and 180°) and (d) CR (30°, 90° and 150°) dimers.

The starting configurations for the dimers were built varying the dihedral angle between the nitrogen atoms (Fig. 2 c, d): **SA** and **SS** (0°, 60°, 120° and 180°), and **CR** (30°, 90° and 150°). All structures were optimized at DFT level with CAM-B3LYP/6-311G (d, p) methodology, adding D3 empirical dispersion. The vibrational frequencies were calculated to confirm the minimum energy structures.

In the second step, nCO₂ molecules were approximated sequentially on both faces of the dimers, with n=2–30 (Fig. 3). Each dimer/nCO₂ structure was optimized keeping the dimer fixed, using the DFTBA method in Gaussian 16 program.

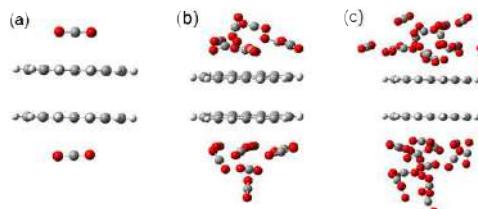


Figure 3. Dimer/nCO₂ structure with (a) n=2, (b) n=16 and (c) n=30.

The aggregation energy (E_{agg}) for all structures was adjusted with counterpoise (Cp) corrections for basis set superposition error (BSSE).

RESULTS: Among some functionals tested, CAM-B3LYP with D3 correction was chosen because it presented E_{agg} in accordance to CCSD calculations for the coronene dimer.⁴ The increasing order of aggregation energy for the coronene dimer is **SA**, **CR** and **SS** (-11.4, -15.4 and -16.2 kcal/mol, respectively). Such result may be attributed to the decrease in the repulsion energy, consequence of the enlargement of the H–H distances.⁵ The presence of nitrogen atoms in 0° (SA and SS) and 30° (CR) decreases E_{agg} , maintaining the same order of the pure coronene dimers (-7.3, -8.6 and -9.6 kcal/mol). In the presence of CO₂, E_{agg} in pure dimer increases linearly (about of 3.4 kcal/mol) as its concentration increases. When N is substituted, **CR** (0°) aggregate follows the same trend observed in pure model. However, in **SA**, this energy decreases smoothly. The calculations for the **SS** (0°) substituted dimers and other arrangements for **SA** and **SS** (60°, 120° and 180°) and **CR** (90° and 150°) are still in progress.

CONCLUSIONS: The presence of N decreases the aggregation energy, independently on the arrangement of aggregate. Nevertheless, in the presence of CO₂ an increase in the strength of aggregation is verified, being in accordance to experimental observations.

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Theoretical study of tautomerization mechanism and drug potential of halogenated Favipiravir compounds for COVID-19 treatment

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Palavras-Chave: COVID-19, Favipiravir, Tautomers.

Introduction

Great efforts have been performed to develop therapeutic options for the treatment of infection caused by the new coronavirus SARS-CoV-2, responsible for the COVID-19. Recently, two proteins of the virus proved to be good potential targets for treatment through their inhibition, the main protease, abbreviated as M^{pro}, and the RNA-dependent RNA polymerase, abbreviated as RdRp^{1,2}. Several antivirals have been studied as inhibitors of these proteins, such as Favipiravir. Due to the high protons' mobility in the Favipiravir structure, it has two tautomeric forms, an enol form and a ketone one³. This work aims to carry out theoretical calculations for the tautomerism process and molecular docking study between the aforementioned proteins and the Favipiravir compounds, for both ketone tautomers (1-F, 1-Cl, 1-Br) and enol tautomers (2-F, 2-Cl and 2-Br).

Methodology

The mechanistic process of the Favipiravir compounds tautomerism and their spectroscopic properties, such as NMR, IR, Raman, EI-MS and UV-Vis were obtained though DFT and B3LYP/6-31G (d, p) level of theory. The M^{pro} and RdRp structures were obtained from the Protein Data Bank with codes 5R82 and 3H5Y, respectively. The molecular docking was conducted with the tool AutoDock Vina, as implemented in the MolAr software.

Results

The tautomerism process occurs via a water-based proton transfer mechanism or without water. A single imaginary frequency was obtained, confirming the achievement of the TS. The tautomerization mechanism without water molecules showed the highest TS energy, -967.84 a.u., this is, less stabilizing energies. Moreover, increasing the number of water molecules in the tautomerism process, it is possible to obtain more stable geometries for the TS structure, making this process energetically more favorable, for instance, with 3 water molecules obtaining -1197.24 a.u. energy value. In addition, molecular docking calculations

were performed. These results are displayed in Table 1.

Table 1. Molecular docking results within the targets.

Compounds	Intermolecular interaction energy (kcal mol ⁻¹)	
	RdRp	M ^{pro}
1-Br	-6.5	-4.4
1-Cl	-6.5	-4.4
1-F	-6.4	-4.8
2-Br	-6.3	-4.6
2-Cl	-6.3	-4.6
2-F	-6.3	-4.7

As we can see, all ligands presented negative intermolecular interaction energies, showing good interaction with both molecular target sites. Our results show that the Favipiravir compounds would be more effective in inhibiting RdRp. Regarding the tautomeric ketone forms, 1-Br and 1-Cl derivatives showed the same interaction energy value, -6.5 kcal mol⁻¹, being more stable than those of the other compounds. This is due to the interactions performed, like hydrogen bonding interactions with Ser300, Asp247, Asp343, Trp246, Asn309, as well as Coulombian interactions with Arg182.

Conclusion

The tautomerism process seems to occur preferentially by a water-assisted mechanism, forming more stable transition states. All molecules have shown RNA-inhibiting properties, generating potential candidates for the COVID-19 treatment. Additionally, we strongly recommend that future in silico studies contemplate both biological targets, which can certainly contribute to the development of new therapies based on the combined use of drugs.

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Structural study of the 1,2,3,4,5-pentamethyl imidazolium - ciclopentadienyl ionic liquid

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Palavras-Chave: *pi-pi stacking; ionic liquid; molecular dynamics simulations*

Bulk ionic liquids (ILs) have been widely studied in the past two decades, both by experimental and computational efforts, due to their large advantages and variety of possible applications [1, 2]. The interplay of electrostatics and dispersive forces, together with hydrogen bonding, controls the complex three-dimensional arrangement of cations and anions in bulk ILs, which reflects in their thermodynamic properties and dynamics [3, 4]. The imidazolium (Im) cation is one of the most explored among the variety of organic cations that might compose ILs, particularly for tailoring the ILs physical properties by different substitutions at the ring moiety [2, 3]. On the other hand, the anion counterpart is commonly rather simple or small, like Cl⁻ or PF₆⁻, or slightly more complex, like [NTf₂]⁻, SCN⁻ or triflate. Our group started to introduce aromatic anions such as the imidazolate

in IL contact pairs [5,6], and, in this work, we present the structure of a bulk 1,2,3,4,5-pentamethyl imidazolium (12345IM) IL with the aromatic cyclopentadienyl anion (C5H₅). Therefore, we performed molecular dynamics computer simulations of 600 ion pairs at a temperature of 360 K applying our IL force field [7,8]. Structural properties are analyzed in terms of radial and spatial distribution functions. The cations and anions were found with shortest distances close to 0.4nm and angles very close to zero between the normal vectors of the anion's and cation's planes (Figure 1). Spatial distributions also demonstrate that cations are distributed preferentially above or below the anion's ring plane confirming the contributions of π⁺-π⁻ stacking interactions between the two aromatic planar ions.

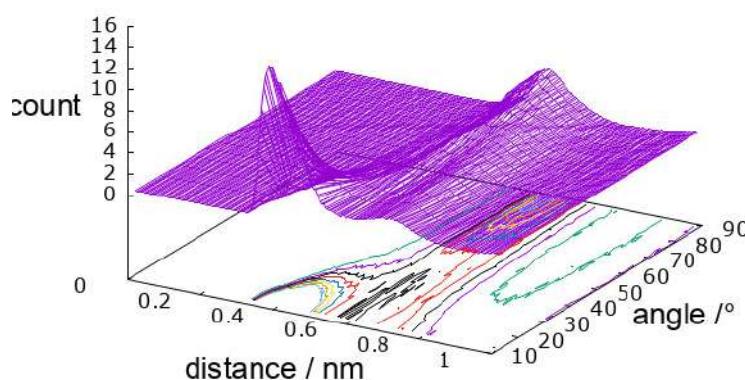


Figure 1. Correlation plot between the RDF and the angles calculated between the normal vectors to the anion and cation's ring planes. The peak at 0.5 nm and angles below 10° demonstrates a parallel orientation of the ions, confirming the presence of π⁺-π⁻ stacking interactions.

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Compressão induzindo modificações em materiais bidimensionais

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Palavras-Chave: diamondeno, bonitrol, materiais 2D

Nos últimos anos a ciência tem observado diversos e inesperados fenômenos advindos dos estudos em materiais bidimensionais (2D). É também importante nessa área a habilidade de criar novos materiais, seja por novas rotas de sínteses ou por transformações químicas e/ou físicas. Em particular, o uso de pressão hidrostática ou uniaxial pode ser usado para revelar novas propriedades desses materiais e para realizar nestes transformações desejadas. Nesse sentido, o estudo desses processos utilizando métodos teóricos pode ser importante para otimizar a busca por condições melhores e otimizadas de realização dos experimentos. Neste trabalho, motivados por resultados experimentais de compressão de bicamada e poucas camadas de materiais 2D, como o grafeno e hBN, com microscopia de força atômica [1-2] e experimentos de espectroscopia Raman com compressão [3-4], estudamos teoricamente as propriedades mecânicas, estruturais e eletrônicas de novos materiais 2D originados a partir de um processo de rehibridização induzida por pressão de camadas de grafeno ou hBN. A metodologia utilizada é baseada em cálculos de primeiros princípios dentro do formalismo da teoria do funcional da densidade como implementado no código SIESTA [5]. Utilizamos pseudopotenciais de norma conservada de Troullier-Martins [6] na forma fatorada de Kleinman-Bylander [7]. Um conjunto de base dupla- ζ composto de pseudofunções atômicas com orbitais de polarização. Uma rede no espaço real é usado com um “mesh cutoff” de 350 Ry. A integração no espaço recíproco foi feita utilizando o esquema proposto por Monkhorst-Pack [8]. Todas as geometrias foram otimizadas de modo que a força máxima em qualquer átomo fosse menor do que 10 meV/Å. Para impor pressão nos sistemas e determinar as pressões de transição nos materiais, utilizamos restrições geométricas nas posições dos átomos durante o processo de otimização da geometria, utilizando um modelo de parede dura nas partes superior e inferior das estruturas (ver Figura 1). Para o caso de bicamadas de hBN, material que é isolante, descrevemos os processos de transformação que levaram a formação de um material 2D condutivo, chamado de bonitrol [1]. Foi possível determinar as pressões de transição de 2 a sete camadas de hBN. Nestes casos as pressões de transição variam de 6.5-8.2GPa.

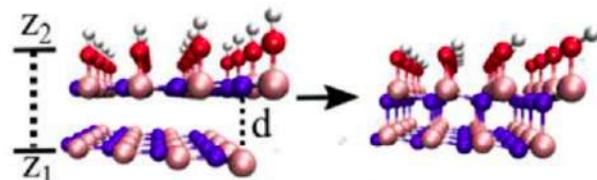


Figura 1: Transformação estrutural na bicamada de hBN. Figura Adaptada de [1].

Uma fenomenologia similar foi empregada para o caso de duas ou mais camadas de grafeno, mas com a formação de um material semicondutor, o diamondeno [2-4]. Para esse caso foi obtido uma pressão de transição da ordem de 11GPa. No estudo das propriedades mecânicas do diamondeno mostramos que seu módulo volumétrico pode variar de 444-466GPa, dependendo do número de camadas, sendo ligeiramente superior ao diamante (423GPa utilizando mesma metodologia). Além disso, encontramos o módulo de Young transversal entre 0.93 – 1.1TPa. Assim, estudamos novos materiais do tipo diamante 2D oriundos da transformação de materiais conhecidos, como grafeno e hBN, e determinamos a relação entre a estrutura eletrônica e as propriedades estruturais dos novos materiais.

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Reações Consecutivas de Dissociação de Hidrogênio da Etilamina no Meio Interestelar

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Palavras-Chave: Etilamina, Acetonitrila, Meio Interestelar .

Introdução. Segundo McGuire,¹ já foram descobertas cerca de 204 moléculas no Meio Interestelar. Dentre essas moléculas, o aminoácido alanina, que é o segundo aminoácido mais simples existente, foi detectado nos meteoritos GRA 95229, LAP 02342, ALH84001 e Nakhla.²

Para entender a formação deste aminoácido é necessário a compreensão da formação e desenvolvimento de seus possíveis precursores.

Experimentos de bombardeamento de átomos de hidrogênio em gelos de acetonitrila sugerem formação de iminas e aminas como produtos,³ que posteriormente podem formar os aminoácidos.⁴

Neste trabalho, deseja-se analisar os caminhos que possam levar à formação da acetonitrila por sucessivas dissociações de hidrogênio da etilamina, na estratégia de uma análise retro-sintética.

Métodos Computacionais. Foram feitos cálculos teóricos, utilizando o programa Gaussian09 adotando o funcional M06-2X e base aug-cc-pVTZ, visando otimizações de geometria, determinação de frequências vibracionais e caminhos de reação.

Resultados. Analisando as energias obtidas, os caminhos observados para a perda de hidrogênio da etilamina são mostrados na figura abaixo.

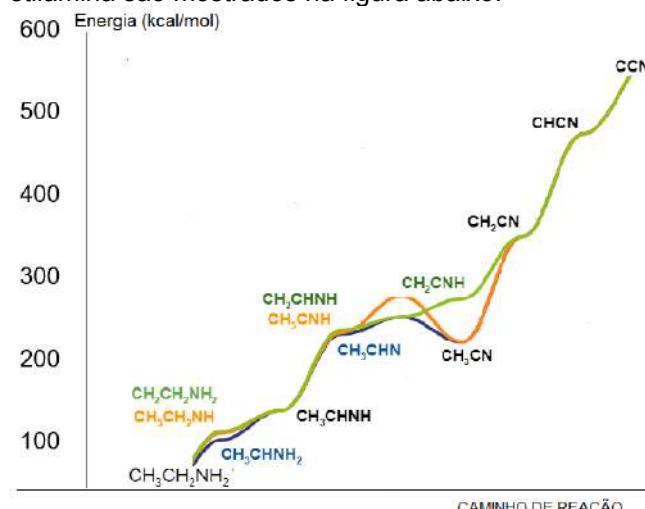
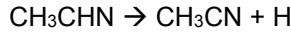
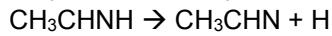
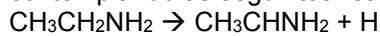


Figura 1 – Caminhos de reação estudados neste trabalho

O caminho em azul é o de menor energia, contemplando as seguintes reações:



Inicialmente, a etilamina perde um átomo de hidrogênio do carbono central, formando uma imina que já foi observada no trabalho de Borget e colaboradores.⁵ Cálculos teóricos DFT feitos por Nguyen, et al.³, evidenciaram a formação do radical CH₃CHN através da hidrogenação da acetonitrila (CH₃CN).

A acetonitrila foi observada pela primeira vez em 1971 por Solomon e Wilson⁶ nos arredores da nuvem molecular Sgr B, sendo um importante intermediário neste mecanismo, formado na última etapa. Dada a evidência de sua disponibilidade em nuvens moleculares e os resultados atingidos neste trabalho, pode-se inferir que ela seria um bom reagente de partida na síntese da etilamina.

O segundo caminho com menor energia é mostrado em laranja e, em verde, é representado o caminho com maior energia. Alguns dos intermediários nestes caminhos já foram observados no meio interestelar, e foram obtidos através de procedimentos experimentais. Os radicais CCN, CHCN e CH₂CN foram detectados nos arredores da estrela de carbono IRC+10216 por Anderson e Ziurys,⁷ Guélin e Cernicharo⁸ e Agundez,⁹ respectivamente. O radical CH₂CNH, tem sido muito estudado e sua detecção foi feita na Sagitarius B2 por Lovas.¹⁰ Baiano e colaboradores estudaram a formação do radical CH₂CHNH, analisando a reação entre NH e CH₃CH₂.¹¹ Dessa forma, os intermediários sugeridos estão em acordo com as observações experimentais.

Conclusões. A observação dos intermediários no ambiente interestelar corrobora com os caminhos de reação propostos neste trabalho. Estudos adicionais para determinação dos coeficientes de velocidade estão em andamento, visando estabelecer um modelo cinético válido em condições astroquímicas.

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Predicting the relative binding affinity of reversible covalent inhibitors

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Keywords: reversible covalent inhibitors, free energy perturbation, halogen bond

Introduction

Covalent inhibitors have received much attention over the past decade by discovering new drugs covalently bound to their targets.¹ In general, the covalent inhibition mechanism is a two-step process wherein involves the formation of a noncovalent complex and, subsequently to the nucleophilic attack, the covalent complex is formed. In this work,² we have used free energy perturbation (FEP) to evaluate the relative binding affinity of eight nitrile-based inhibitors (Fig. 1) of human Cathepsin L (hCatL) in both covalent and noncovalent states.

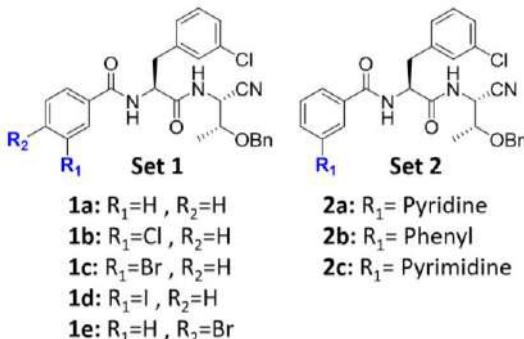


Figure 1: 2D structural representation of hCatL reversible covalent inhibitors. They were divided into two groups according to their chemical characteristics.

Methodology

All the molecular dynamics simulations and relative binding free energy (RBFE) calculations were carried out through AMBER18. The strategy used here was a stepwise *decharge-vdW-recharge* process with the **1a** and **2a** compounds taken as reference. The transformations were performed in the protein and water environment for both covalent and noncovalent states. For the P3-halogenated compounds at *meta* position, an extra-point (EP) of positive charge was applied in the recharge step in order to represent the so-called sigma-hole.³

Results

The RBFE values were estimated using the Zwanzig relationship and results for $\Delta\Delta G_{noncov}$ and $\Delta\Delta G_{cov}$ are shown in Table 1. FEP results reveal a strong correlation (Pearson's correlation, r , of 0.86, Fig. 2a) between the experimental data and RBFE for covalent state. In contrast, there is a modest correlation between the free energy changes determined for the noncovalent state and the experimental data ($r=0.69$; Fig. 2b). Furthermore, the mean unsigned error (MUE) is reduced from 1.33 to

0.92 kcal mol⁻¹ for the $\Delta\Delta G_{noncov}$ and $\Delta\Delta G_{cov}$, respectively.

Table 1: RBFE values (kcal mol⁻¹) calculated for the noncovalent ($\Delta\Delta G_{noncov}$) and covalent ($\Delta\Delta G_{cov}$) states.

Transformation	Mutation	$\Delta\Delta G_{exp}$	$\Delta\Delta G_{noncov}$	$ \Delta X _{noncov}^a$	$\Delta\Delta G_{cov}$	$ \Delta X _{cov}^a$
1a → 1b	H → Cl	-0.9	-2.5	1.6	+1.3	2.2
1a → 1c	H → Br	-1.7	-2.0	0.3	-0.4	1.2
1a → 1d	H → I	-1.9	-1.9	0.02	-0.9	1
1a → 1e	H → p-Br	-0.1	-0.9	0.7	-0.3	0.1
2a → 2b	N → CH	+2.4	-1.3	3.6	+3.1	0.7
2a → 2c	CH → N	+1.7	0.0	1.7	+1.5	0.2

^aAbsolute error between the calculated and experimental values

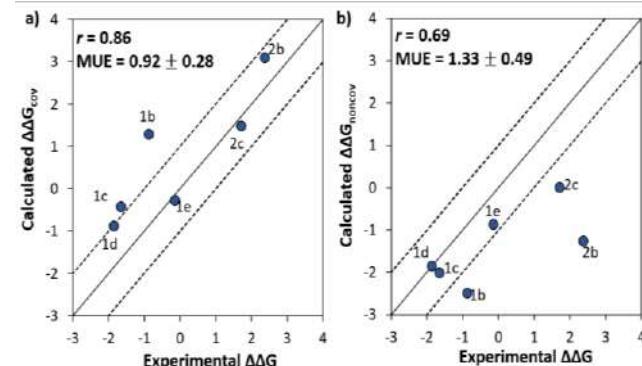


Figure 2: Comparison of the free energy changes (kcal mol⁻¹) obtained for alchemical transformations in (a) the noncovalent and (b) the covalent state with the experimental relative binding affinities.

In addition, all binding modes were determined and rationalized to explain the observed potency, and, for the set **2** of compounds, hydration free energy calculations were also carried out.

Conclusions

The results obtained for the covalent state present a good correlation with the experimental data, and the ligands can be ranked with high accuracy. Hence, it is assumed that the covalent complex is more relevant for the binding free energy than the noncovalent complex. For the halogenated compounds participating in a halogen bond, an EP should be used in the recharge step. Overall, the protocol employed in this work can be a powerful tool in the development of new covalent drugs.

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Estudo teórico de um quimiodosímetro cromogênico na detecção de diferentes ânions: análise espectral e termodinâmica

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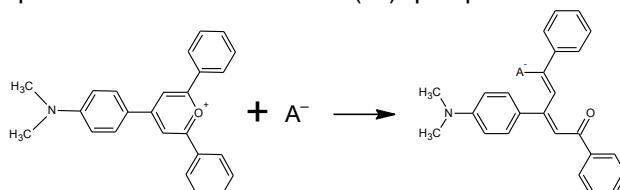
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Palavras-Chave: quimiodosímetros cromogênicos, detecção de ânions, UV-VIS.

Introdução

Os quimiodosímetros são sensores moleculares que possibilitam a detecção óptica de espécies químicas. Em seus estudos, Jiménez e colaboradores¹ observaram que quando um derivado do cátion 2,4,6-triaril-pirílio portando um grupo dimetilamina em um dos anéis arilas (Figura 1) está em uma solução água:acetonitrila (1:1 v/v), especificamente na presença do ânion sulfeto, há uma mudança na coloração da solução de magenta para azul.

Figura 1. Esquema genérico da reação entre o quimiodosímetro e um ânion (A^-) qualquer.



Este trabalho busca um melhor entendimento² do comportamento do quimiodosímetro estudado na presença de diferentes ânions: OH^- , SH^- , F^- , Cl^- , CN^- , Br^- e NO_3^- .

Metodologia

Todos os cálculos foram realizados através do software Gaussian 09W³ em nível B3LYP/6-31+G(d). Os espectros UV-VIS foram obtidos através da Teoria do Funcional de Densidade Dependente do Tempo (TD-DFT) no mesmo nível de teoria. No intuito de uma melhor representação do meio, utilizou-se o modelo de solvatação PCM para representar os solventes acetonitrila e água.

Resultados e Discussão

A Figura 2 apresenta os espectros com os máximos de absorção ($\lambda_{\text{máx}}$, em nm) calculados para os reagentes e produtos da reação (Figura 1) entre o quimiodosímetro estudado com diferentes ânions, em acetonitrila e água. Observa-se um deslocamento dos máximos de absorção da região do ultravioleta para a região do visível, nas reações com a presença de nucleófilos fortes como OH^- , SH^- , F^- e CN^- . Uma maior estabilidade eletrônica também é observada com esses mesmos íons, Figura 3.

Figura 2. Espectros calculados para os reagentes (esquerda) e produtos (direita) da reação estudada (Figura 1), em acetonitrila e água.

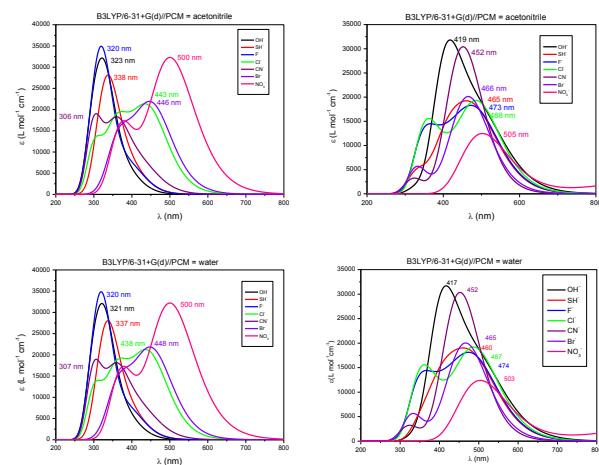
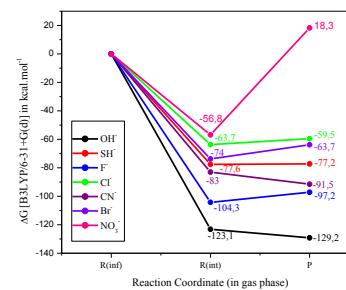


Figura 3. Perfil de energia livre da reação estudada (Figura 1) em fase gasosa.



Considerações Finais

Uma breve análise termodinâmica demonstrou um menor favorecimento energético na interação do quimiodosímetro com ânions maiores (NO_3^- , Cl^- e Br^-). Além disso, apenas os ânions com maior poder nucleofílico (OH^- , SH^- , F^- e CN^-) foram capazes de deslocar as bandas de absorção da região do ultravioleta para a região do visível.

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Propriedades estruturais, mecânicas e eletrônicas do SrTiO₃ dopado com Ag

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Palavras-Chave: SrTiO₃, prata, TFD.

1. Introdução

O SrTiO₃ (STO) é um semicondutor do tipo n com estrutura cúbica simples, com energia de *band gap* indireta de aproximadamente 3,2 eV à temperatura ambiente¹. A natureza indireta do *band gap* envolve a transição do elétron da banda de valência para a banda de condução via fônon e, portanto, parte da energia incidente é desperdiçada nessas transições, sendo necessária a dopagem com metais de transição e consequentemente a prata (Ag) se torna um bom candidato para dopagem tendo em vista suas propriedades espectroscópicas a luz visível e suas propriedades antimicrobianas².

2. Procedimentos computacionais

As simulações via teoria do funcional de densidade foram realizadas usando o funcional híbrido PBE0 implementado no programa CRYSTAL17 com funções de base do tipo gaussiana³. As funções de bases adotadas são: HAYWSC-311(d11f)G, TZVP, e O_8-41 e Ag para Sr, Ti, O e Ag, respectivamente.

3. Resultados e discussões

A simulações subestimam a energia do *band gap* em 0,08 eV, os parâmetros de rede estão em consonância com o valor experimental de 3,9 Å. A substituição de 12,5% de Sr por Ag (SATO) (1:1) aumentou 0,21 eV a energia do “*band gap*” da estrutura STO (Tabela 1). Para estruturas cúbicas só existem três constantes elásticas a serem determinadas C₁₁, C₁₂ e C₄₄. O modulo volumétrico, B₀, para um sistema cúbico pode ser calculado: B₀=(C₁₁ + 2C₁₂)/3. A dopagem com Ag promove a redução nas constantes C₁₁ e C₄₄ ocasionando maior deformação no eixo x e nos planos xOy e xOz, promoveu o aumento da constante C₂₂ resultando em menos deformação nos eixos x e y (Figura 1).

Tabela 1 - Parâmetro de rede e “band gap”.

	STO*	SATO*	STO – Experimental ⁴	STO	SATO
a(Å)	3,91	3,88	3,90	3,94	3,91
E _{gap} (eV)	3,12	3,19	3,20	1,99	1,87

A dopagem com Ag no STO alterou a energia do *band gap*, passando de gap indireto (R – Γ) para direto (Γ – Γ) (Figura 1a e 1b). Abaixo do nível de Fermi as interações predominantes são entre Ag – O no mínimo da banda de condução ocorrem majoritariamente as interações Ti – O. Os resultados de densidade de estados (DOS),

mostram que o atomo de oxigenio detem a maior densidade eletrônica na banda de valência em ambas estruturas.

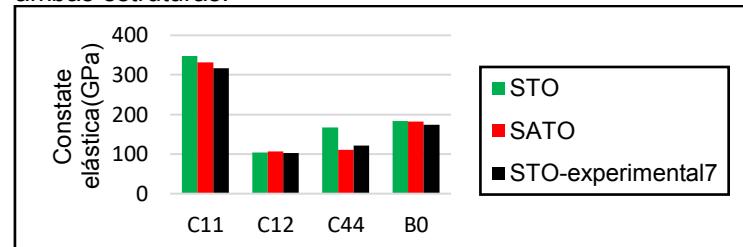


Figura 1 - Constante elástica e modulo volumétrico.

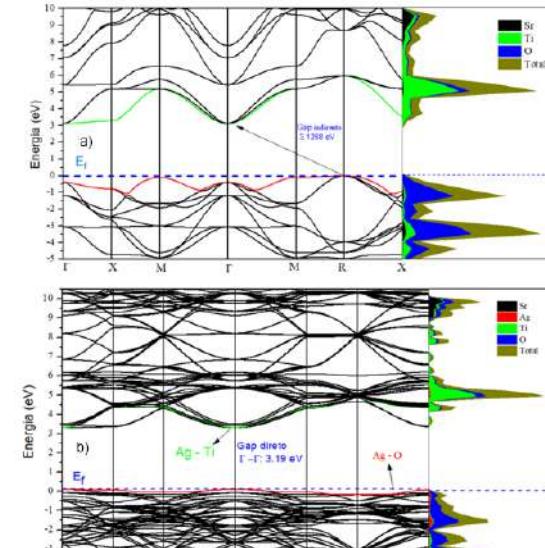


Figura 2 - Estrutura de Bandas e DOS: a - STO; b – SATO.

4. Conclusão

O modelo mostrou bons resultados para o material na substituição Sr por Ag. A dopagem promoveu desordem a curto alcance resultando em deformações elásticas e na modificação da natureza da energia do *band gap* de indireta para direta, tornando o material mais eficiente em aplicações ópticas.

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Study of the halon C₂BrClF₄, reaction rate and properties

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Keywords: Halons, 1-Bromo-2-Chlorotetrafluoroethane (*R*-114B1), Reaction rate

INTRODUCTION

The group of halogenated organic compounds are extensively used as pesticides, anesthetics, fire extinguishers, refrigerants, etc¹. In our knowledge, there is no reference data to several of them, mainly the halon 1-Bromo-2-Chlorotetrafluoroethane (C₂BrClF₄), that is the object of this work.

In this work we present three geometry variations for the C₂BrClF₄ and the respective reaction rates with H₂.

METHODS

For the *ab initio* calculations we used B3LYP/6-311g(2d,d,p) method for frequencies and geometries, internal to CBS-QB3 which computes very accurate energies. All calculations were performed using GAUSSIAN09 program and the rate constant via APUAMA^{2,3}.

RESULTS

All the three geometry variations for C₂BrClF₄ (named V1, V2 and V3) was reacted with H₂, in all cases we obtained, as result of the reaction, different geometries of C₂HBrClF₃ + HF as shown in figure 1.

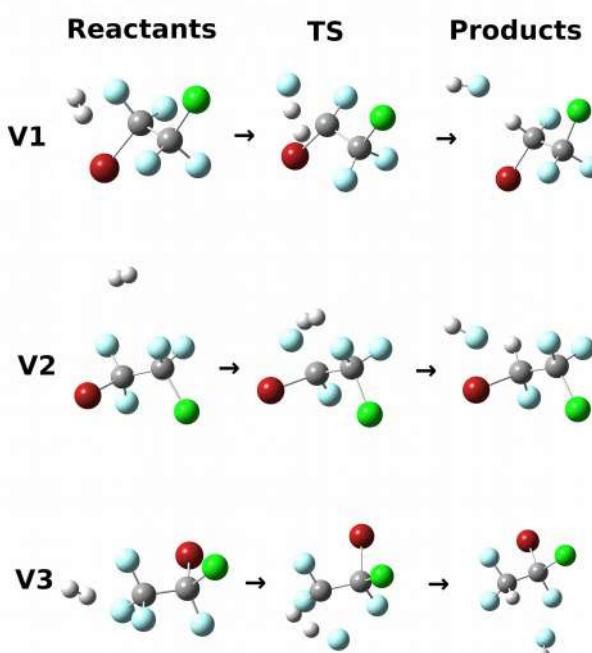


Figure 1: Reaction schematic for the three variations of the C₂BrClF₄

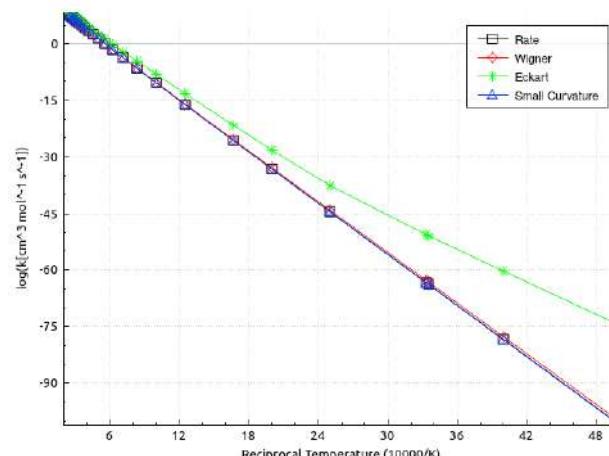


Figure 2: Reaction rate of (V1) C₂BrClF₄ + H₂ via APUAMA

For all three C₂BrClF₄ + H₂ reactions the thermodynamic properties, such as, entropy, enthalpy and heat capacity was calculated, and the rate constant with Wigner, Eckart and small curvature tunnelling corrections were obtained via APUAMA , as shown in figure 2 for V1 variant.

CONCLUSION

The three reaction rates were obtained and written as Arrhenius form:

$$k_{(V1)}(cm^3 mol^{-1} s^{-1}) = 5.22 \times 10^4 T^{2.37} \exp(1.01 \times 10^5 / RT)$$

$$k_{(V2)}(cm^3 mol^{-1} s^{-1}) = 1.28 \times 10^5 T^{2.39} \exp(1.00 \times 10^5 / RT)$$

$$k_{(V3)}(cm^3 mol^{-1} s^{-1}) = 1.06 \times 10^6 T^{2.31} \exp(2.73 \times 10^5 / RT)$$

We can observe that V1 rate is faster than V2 which is faster than that of V3, and the barriers of V1 and V2 are energetically equivalent.

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Mecanistic study of the ROCOP reaction of CHO and CO₂ catalysed by a Mg(II)Mg(II) catalyst

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Keywords: Catalysis, Magnesium, CO₂.

Introduction

Several human activities are responsible for the emission of CO₂ that is causing the intensification of the Greenhouse Effect. Therefore, technologies devoted to mitigate the emissions of this gas or its re-utilization are of great importance. In this aspect, the catalytic transformation of the CO₂ and cyclohexene oxide (CHO) into copolymers or cyclic carbonates – like the *cis*-cyclohexene carbonate – by the ring opening and copolymerization (ROCOP) is a good alternative to convert CO₂ into valuable products.^{1,2} In this regard, we proposed to study computationally the reaction mechanism of the ROCOP between CO₂ and CHO catalysed by a Mg(II)Mg(II) catalyst.

Methodology

The energetic profile was studied at the BP86/Def2-SVP/SMD level of theory, using dibutyl ether as implicit solvent. All calculations were performed in ORCA 4.2.

Results

The energetic profile of the reaction is presented in figure 1. In red are the steps relative to the path a – formation of the polymer – and in green the path b – *cis*-cyclohexene (*cis*-CHC) formation. The first step is the CHO ring opening step having a ΔG^{\ddagger}_{TS} of 62.5 kJ·mol⁻¹. The structure of *TS*₁ is shown in figure 2. Overall, The passage of *I*₁ to *I*₂ is a exergonic step, leading to an endergonic step to the formation of *I*₃ (conformational change before the coordination of CO₂ in *I*₄).

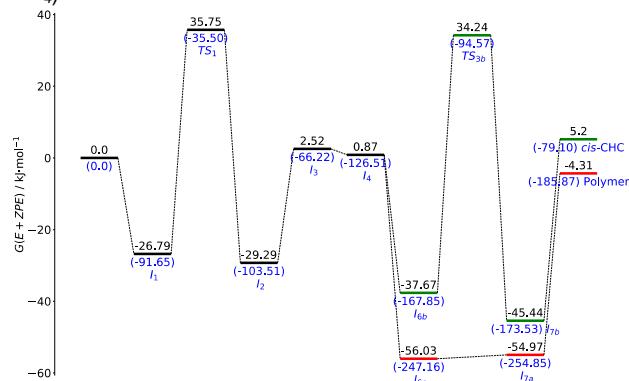


Figure 1. Energetic profile of the reaction.

The formation of the polymer described in path a is more thermodynamic favored as would be expected due to entropy contributions. The path b is less

favored, in which $\Delta G^{\ddagger}_{TS\ b} = 71.9$ kJ·mol⁻¹. In figure 3 is presented the *TS*_{3b} structure.

As can be seen in the energetic profile, the thermodynamic product is the polymer, even though the barrier to the formation of the *cis*-cyclohexene carbonate is feasible.

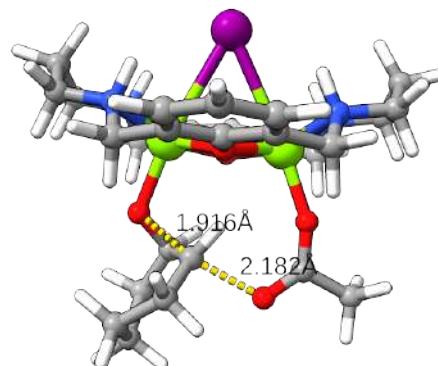


Figure 2. Transition state 1 (*TS*₁) structure. In white, grey, blue, red, yellow and purple are H, C, N, O, Mg and I atoms, respectively.

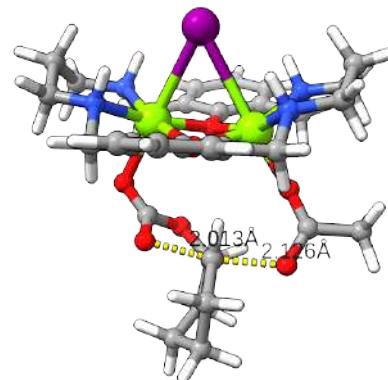


Figure 3. Transition state 3b (*TS*_{3b}) structure.

Conclusions

In conclusion, the ROCOP reaction of CHO and CO₂ catalyzed by the Mg(II)Mg(II) studied catalyst is feasible to take place, in which the polymer is the most favorable product.

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Revisiting the electronic structure of the first alkoxide containing titanium and iron

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Keywords: DFT, alkoxides, iron titanium compounds

Introduction

Alkoxides of transition metal ions rouse interest due to their applications in the research of new electronic devices and biocompatible oxide materials.¹ The first titanium and iron polynuclear isopropoxide $[FeCl\{Ti_2(O^{\prime}Pr)_9\}]$ (**A**)² has been used as a mixed-metal single-source precursor of the pseudobrookite Fe_2TiO_5 and as a metal-friendly catalyst for the preparation of biodegradable polymers as polylactide and polycaprolactone.^{3,4} Our previous studies using semiempirical quantum mechanical calculations (ZINDO/S) were consistent with an $S = 2$ ground state.² Herein, the electronic structure of **A** was revisited using Density Functional Theory (DFT).

Methods

All calculations were performed with Gaussian16³ using the B3LYP⁶ density functional and LANL2DZ⁷ as the basis set. Molecular spin states ($2S+1$), varying from 1 until 7, had their SCF energies calculated using x-ray diffraction data as a predefined geometry for **A**. In the sequence, coordinates were optimized for each molecular spin state, and corresponding energies were recalculated. For the electronic ground state, Bader's charge and the molecular electrostatic potential surface (EPS) were obtained using the Multiwfn code.⁸

Results

The respective SCF energies for single point and optimized molecular geometries are shown in Table 1.

Table 1. Relative energies for spin states of **A**

$2S+1$	Energy (single point) / (kJ mol ⁻¹)	Energy (opt.) / (kJ mol ⁻¹)
1	189.65	156.36
3	107.20	99.50
5	0.00	0.00
7	307.99	210.07

The low relative squared deviations from experimental crystallographic data, with errors of 1.12% ($S = 2$) and 5.76% ($S = 3$), confirm the optimization of geometries. The minimum of energy was found for $S = 2$, confirming the quintet as a ground electronic state and indicating the presence of a high-spin iron(II) center. Atomic Bader's charges calculated for the main core of **A** are depicted in Fig. 1. Electron densities are greater around the iron(II) than on titanium(IV) centers. Regarding only negative charges on oxygen atoms of isopropoxide ligands, μ_3 -OR > μ_2 -OR > O_{terminal}.

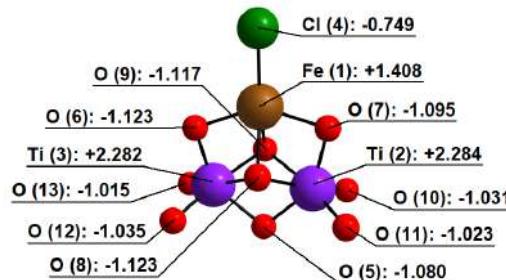


Figure 1. Main core and Bader's atomic charges for **A**. The C and H atoms were omitted for clearness

Also, the EPS was generated for the quintet with $S=2$ (Fig. 2). The regions close to the carbon frame, colored in red, are deficient in electron density.

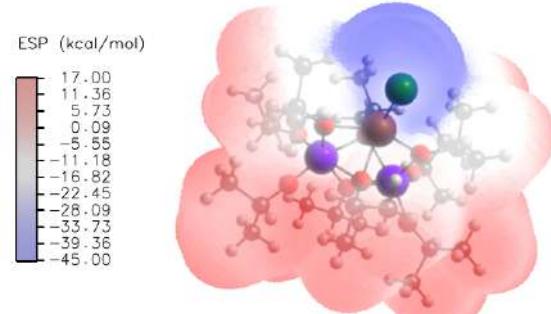


Figure 2. Electrostatic Potential Surface for compound **A**.

The region around the Cl center exhibits a high density of negative exposed charges. The spin difference map (not shown) displayed a localized spin density encompassing the Fe(1) center, as expected for a high-spin iron(II) center.

Conclusions

The predicted quintet state, $S = 2$ for **A**, is in accordance with our previous results using ZINDO/S and with the crystallographic data. The DFT approach at B3LYP/LANL2DZ level was employed to describe the electron densities and charges distribution accurately in this heterometallic alkoxide.

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Combinação do Dp4+ e Rede Neural (ANN-PRA) com Fatores de Escalonamentos de Deslocamentos Químicos de RMN de ^{13}C e ^1H (baseados em Regressões Lineares) para Auxiliar na Determinação Estrutural do Elemol

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Palayras-Chave: *Elemol. Dp4+.* ANN-PRA.

Introdução

A determinação estrutural das moléculas é de fundamental importância na química orgânica moderna.¹ Para obter a determinação estrutural utiliza-se em grande escala a Ressonância Magnética Nuclear (RMN), sendo o deslocamento químico (δ) o parâmetro mais importante.¹ Este é um trabalho teórico-experimental, onde a molécula foco do estudo é o elemol (figura 1), e seus diastereoisômeros um sesquiterpeno isolado da espécie *Eryngium glaziovianum* L. (Apiaceae), que apresenta atividades farmacológicas e biológicas.² Essa molécula foi isolada e aqui apresentamos a sua caracterização experimental e teórica por meio de dados de RMN de ^{13}C e ^1H e a possível confirmação da estrutura utilizando as ferramentas rede neural (ANN-PRA)³ e Dp4+.⁴

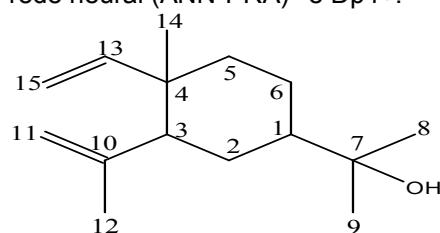


Figura 1. Estrutura do elemol

Resultados e Discussões

Os cálculos de δ de RMN de ^{13}C e ^1H para o elemol e seus diastereoisômeros foram realizados em nível GIAO-mPW1PW91/6-31G(d)/mPW1PW91/6-31G(d). Todos os cálculos teóricos foram realizados em fase gasosa, exceto os utilizando para ferramenta de rede neural ANN-PRA, onde utilizou o método contínuo para simular os efeitos de solvente PCM (modelo contínuo polarizável) com clorofórmio deuterado, o mesmo solvente utilizado para se obter os dados experimentais. Aplicaram-se os fatores de escalonamentos para ^{13}C e ^1H , compararamos os valores de desvio médio absoluto (MAD) e desvio médio quadrático (RMS). Dos 4 diastereoisômeros o elemol apresentou o menor valores de MAD e RMS escalonado para ^{13}C (MAD: 1,71 ppm e RMS: 2,02 ppm), e ^1H (MAD: 0,20 ppm e RMS: 0,27 ppm). Utilizamos a ferramenta Dp4+ baseada em

probabilidades com 16 parâmetros para cada nível de teoria usado: oito para as distribuições ^{13}C (vscal, oscal, vu-sp², mu-sp², σu-sp², vu-sp³, μu-sp³, e σu-sp³), oito parâmetros correspondentes para o 1 Série H.¹ O Dp4+ foi utilizado para diferenciar e confirmar a estrutura do elemol dos seus diastereoisômeros, com base nos dados obtidos pelos descritores (sDP4+, uDP4+ e DP4+) para C e H, no qual fez a confirmação da estrutura do elemol. A ferramenta ANN-PRA identificou que a estrutura isolada corresponde à do elemol.

Conclusões

De acordo com os resultados dos cálculos teóricos e dados experimentais, combinados com as ferramentas rede neural (ANN-PRA) e Dp4+, foi feito a confirmação da estrutura do elemol. A combinação dessas ferramentas juntamente com protocolos de escalonamento de ^{13}C e ^1H , são métodos poderosos de baixo custo computacional e de grande valia para confirmar as estruturas de produtos naturais.

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Reação do Ânion Amideto com o Formiato de Metila em Fase Gasosa: Um Estudo Quântico Computacional do Perfil de Energia Potencial

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Palavras-Chave: Formiato de metila, Amideto, Mecanismo de reação.

INTRODUÇÃO

As reações de formiato de alquila com nucleófilos desempenham um papel central em um grande número de processos bioquímicos.^[1] É bem estabelecido que essas reações podem ocorrer por caminhos de reação competitivos (ver Figura 1) e a formação dos produtos está sob o controle cinético. A reação entre o íon amideto (NH_2^-) com o formiato de metila (HCOOCH_3) em fase gasosa leva a formação de vários produtos iônicos que foram identificados experimentalmente,^[2] porém, nada se sabe sobre perfil de energia potencial dessa reação bem como a relação das barreiras de ativação para explicar a distribuição dos produtos. Para preencher essas lacunas, o objetivo deste trabalho está em explicitar a relação entre estrutura, reatividade e energia nos caminhos de reação que levam à formação dos produtos.

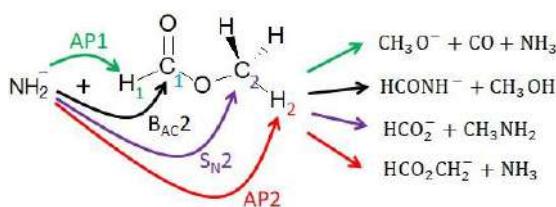


Figura 1: Caminhos de reação da reação $\text{NH}_2^- + \text{HCOOCH}_3$

MÉTODOS

O programa GaussView foi utilizado para visualização das estruturas moleculares e o Gaussian 09 para os cálculos de estrutura eletrônica. O método B2PLYP-D3 com a função de base aug-cc-pVDZ foram utilizados para caracterizar todos os pontos estacionários do mecanismo de reação. Para todos os estados de transição foi feito o cálculo IRC para encontrar as respectivas estruturas de mínimo.

RESULTADOS

Na Figura 2 está o perfil de energia potencial de cada caminho reacional. Observar-se que a interação entre os reagentes pode levar a formação de dois complexos: RC1 e RC2. Após o RC1 há dois estados de transição competitivos TS1 e TS2. O TS1 corresponde a um ataque nucleofílico no carbono “2” ($\text{S}_{\text{N}}2@\text{C}2$) que leva à formação dos produtos $\text{HCO}_2^- + \text{CH}_3\text{NH}_2$. O TS2 trata de um mecanismo de abstração do próton “2” (AP2) antes da formação dos produtos $\text{HCO}_2\text{CH}_2^- + \text{NH}_3$. Outro possível caminho é

um rearranjo pelo TS3 formando um intermediário tetraédrico Int1 pelo caminho $\text{B}_{\text{AC}2}$, que após o TS4 forma o íon $\text{HCONH}^- + \text{CH}_3\text{OH}$. Esse último produto também pode ser formado a partir do RC2 através do caminho $\text{S}_{\text{N}}2@\text{C}1$. Por fim, os produtos $\text{CH}_3\text{O}^- + \text{CO} + \text{NH}_3$ são formados pelo caminho AP1. A proporção experimental para a formação dos íons HCO_2^- é de 17% contra 83% para HCONH^- . Observa-se que barreira de ativação do TS3 (3,3 kcal/mol) é menor que do TS1 (5,2 kcal/mol), indicando que o caminho $\text{B}_{\text{AC}2}$ deve ser favorável em relação ao caminho $\text{S}_{\text{N}}2@\text{C}2$.

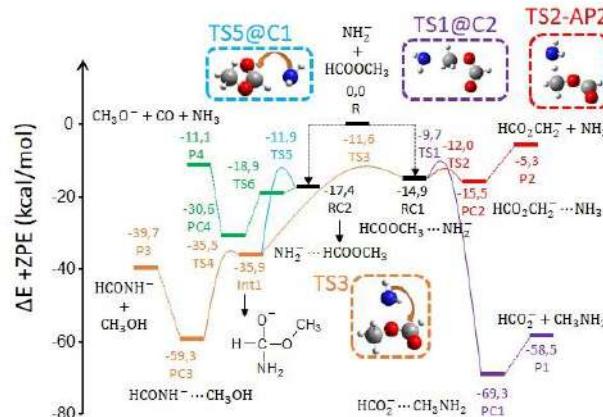


Figura 2: Perfil de energia potencial no nível B2PLYPD3/aug-cc-pVDZ.

CONCLUSÕES

Os resultados obtidos neste trabalho fornecem um entendimento detalhado do mecanismo da reação $\text{NH}_2^- + \text{HCO}_2\text{CH}_3$, para explicar à formação majoritária do produto iônico HCONH^- . A combinação destes resultados com os cálculos estatísticos RRKM está em execução, bem como o estudo da microsolvatação desta reação, para estabelecer o papel do solvente nas mudanças das distribuições dos produtos.

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Estudo Teórico da Fotodissociação do Clorometano Mono-hidratado

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Palavras-Chave: Cloreto de metila; canais fotodissociativos; métodos multiconfiguracionais

Introdução

O CH₃Cl apresenta grande abundância atmosférica, uma vez que possui origem natural e antropogênica. Assim, contribui de maneira significativa na degradação da camada de ozônio.

Visto que a molécula de água está presente em grande quantidade na atmosfera, esta é capaz de interagir com a molécula de clorometano influenciando os seus caminhos fotodissociativos. A formação do complexo CH₃Cl(H₂O) foi demonstrada experimentalmente por Dozova (2005)¹.

Este trabalho busca avaliar, através de métodos multiconfiguracionais e multireferência (MCSCF e MR-CISD), a influência da molécula de água sobre a fotodissociação do CH₃Cl, procurando caracterizar o estado iônico para o complexo CH₃Cl(H₂O), bem como possíveis canais de dissociação iônicos.

Procedimentos Computacionais

Efetuou-se, inicialmente, um cálculo de otimização para o complexo CH₃Cl(H₂O) a nível MR-CISD com base aug-cc-pVDZ. Posteriormente, identificou-se o estado iônico ao longo da coordenada de dissociação carbono-cloro, cuja estrutura foi otimizada também a nível MR-CISD. A estrutura do par iônico permitiu verificar a existência de dois distintos canais iônicos, sendo estes o canal A, onde são gerados um metanol protonado ([CH₃-OH₂]⁺) e um cloreto, e o canal B onde forma-se um cloreto hidratado (Cl...HOH) e um cátion metil. Os fragmentos destes canais também foram otimizados. Para obter as energias relativas dos sistemas estudados efetuou-se cálculos de estados (single point), tabela 1. Para a realização dos cálculos utilizou-se o programa COLUMBUS 7.0.

Tabela 1 - Orbitais de valência do espaço ativo (CAS) e orbitais de Rydberg auxiliares (AUX) usados no cálculo de estados (Valência + Rydberg) a nível MR-CISD com base d-aug-cc-pVDZ(C)/aug-cc-pVDZ(Cl,H,O).

Sistema	CH ₃ ⁺ (H ₂ O)Cl ⁻	Cl...HOH + CH ₃ ⁺	[CH ₃ -OH ₂] ⁺ + Cl ⁻
CAS	os três n(Cl) ^a , e 2p _g (C), 3s(C) (AUX)		
Estados	7A (4A) ^b	5A'+2A'' (5A') ^b	5A'+2A'' (5A') ^b

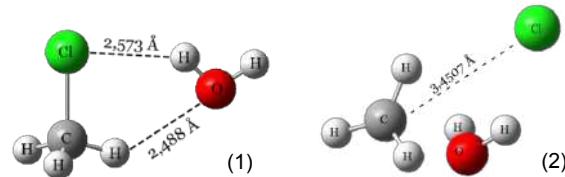
^aOrbitais n(Cl) correspondem a orbitais não ligantes do cloro; ^bOs estados destacados em parênteses correspondem aos estados de interesse.

Resultados

Identificou-se uma estrutura de mínimo para o complexo CH₃Cl(H₂O), figura 1. Essa possui simetria C_s e apresenta em sua estrutura molecular

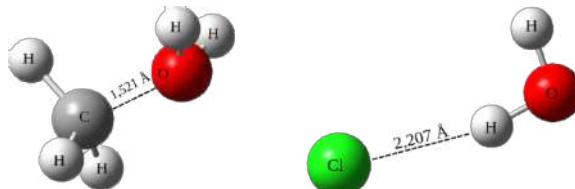
duas ligações de hidrogênio. Compara-se a estrutura do par iônico caracterizado com a estrutura do CH₃Cl(H₂O) no estado fundamental na figura 1. Assim, verifica-se no par iônico uma forte influência do solvente. O estado iônico localiza-se 4,24 eV (MR-CISD+Q) acima do estado fundamental.

Figura 1 – Comparação entre estrutura do estado fundamental (1) e par iônico (2).



Em relação ao CH₃Cl isolado², caracterizou-se dois canais iônicos adicionais ([CH₃-OH₂]⁺ + Cl⁻ (A) e Cl...HOH + CH₃⁺ (B)). Os principais fragmentos iônicos destes canais estão apresentados na figura 2. As energias de ligação destes respectivos canais em relação ao par iônico são de 2,40 eV e 4,38 eV.

Figura 2 – Estruturas otimizadas a nível MR-CISD/aug-cc-pVDZ dos íons [CH₃-OH₂]⁺ e Cl...HOH.



Conclusões

A presença de solvente na dissociação do clorometano pode influenciar em uma maior geração de íons, reduzindo a produção de radicais cloro. Entretanto, é necessário uma melhor análise sobre o rendimento reacional de tais canais.

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Agradecimentos





Diversidade estrutural em cátions oriundos de moléculas aromáticas

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Palavras-Chave: cátions, HPA, astroquímica

Introdução

Com as recentes detecções da benzonitrila, naftonitrila e ciano-ciclopentadieno na nuvem molecular Taurus 1 (TMC-1) a busca por moléculas aromáticas foi bastante intensificada no meio interestelar. Além das detecções, outro grande desafio é propor redes de reações para a formação de moléculas cíclicas que descrevam corretamente a abundância de diversos produtos. Porém, é preciso mapear as possibilidades de formação de diferentes isômeros para uma adequada proposta de mecanismos de formação. Além disso, moléculas aromáticas, em especial os hidrocarbonetos policíclicos aromáticos (HPAs), são consideradas importantes carreadoras de bandas interestelares difusas auxiliando na identificação das bandas de emissão na região do infravermelho.

Um desafio na busca de isômeros de baixa energia para moléculas são as influências do estado de carga e do grau de hidrogenação. O aumento de carga pode causar rearranjos na estrutura levando a geometrias pouco usuais como o caso do dicáton de benzeno e da bifenila. No primeiro exemplo, a estrutura mais estável é piramidal pentagonal¹ enquanto no segundo é uma estrutura do tipo acenafteno². Por sua vez, a diminuição do número de átomos de hidrogênio pode causar um severo rearranjo da estrutura¹. Dessa forma, métodos automatizados para explorar o espaço das conformações são desejáveis uma vez que a intuição química pode falhar.

O objetivo desse trabalho é utilizar buscas automatizadas e guiadas de novos isômeros de íons e radicais oriundos de moléculas aromáticas utilizando diferentes níveis de cálculo. Além disso, quando pertinente, propriedades estruturais e espectroscópicas assim como o espectro na região serão infravermelho serão simulados. Espera-se que o conjunto de resultados obtidos auxilie na identificação de novas moléculas assim como na busca de mecanismos de formação.

Métodos

A busca automatizada por novas estruturas geradas a partir de pequenos aromáticos serão realizadas utilizando o método de algoritmo genético (GA) implementado no programa AUTOMATON em nível DFT utilizando o funcional PBE0. Esse protocolo foi validado em um trabalho recente¹. Para sistemas

maiores, o espaço químico será explorado utilizando o algoritmo de metadinâmica combinado com o método *extended tight binding* GFN2-xTB, ambos implementados no programa xTB. Após a seleção de estruturas, cálculos em nível DFT (PBE0/def2-TZVP) serão realizados no programa ORCA para simular os espectros e demais propriedades. Cálculos de frequências vibracionais serão realizados nas estruturas de baixa energia para comprovar que são mínimos na superfície de energia potencial.

Resultados prévios

O mínimo global (GM) do dicáton do benzeno (estrutura piramidal pentagonal) foi obtido aplicando o GA. Essa estrutura foi reotimizada em nível PBE0/def2-TZVPP¹ (Figura 1(a)). O GM do dicáton do naftaleno foi obtido utilizando a busca por metadinâmica com um total de 10 trajetórias de 500 ps em nível GFN2-xTB. A estrutura foi reotimizada em nível PBE0/def2-TZVP³ (Figura 1(b)). Por fim, o GM do dicáton da bifenila foi obtido por busca guiada utilizando a mesma base e funcional².

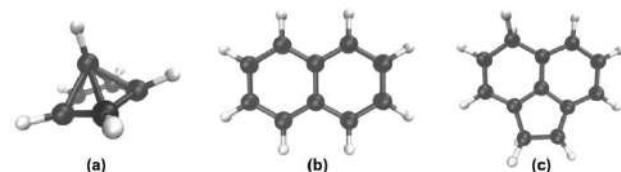


Figura 1 - Mínimo global de dicátions selecionados.

Conclusões parciais

Para diferentes arquétipos de moléculas aromáticas obtiveram-se distintas estruturas para o mínimo global. Para o naftaleno a estrutura do dicáton é similar a do neutro enquanto benzeno e bifenila apresentam geometrias completamente distintas.

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Calculation of Raman spectra using VSCF/VCI wave functions

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Keywords: anharmonic Raman spectrum, Coupled Cluster electronic structure, vibrational self-consistent field method

In this study, the vibrational Raman spectrum of molecular systems (H_2O , C_2H_2 and CH_4) was computed using anharmonic wave functions from the Vibrational Self-Consistent (VSCF) method.[1] As VSCF is an independent particle model, vibrational wave functions were further refined through Configuration Interaction (VCI) calculations. In the hereby presented computations, the vibrational Hamiltonian includes vibrational angular momentum contributions and the Potential Energy Surface (PES) is represented either by: (i) a forth order Taylor expansion or (ii) numerically, through a 3-mode [1] representation. The excitation radiation (laser frequency) selected to obtain the Raman spectra of those molecules matches the so-called *far-from-resonance* regime, thus transition polarizabilities were described according to Placzek's theory. The electronic Polarizability Surface (PS) was represented by a second order Taylor expansion where the first and second order geometric derivatives of the dynamic polarizabilities were evaluated using finite difference formulas. The electronic structure calculations were performed at the CCSD(T)/aug-cc-pVQZ (PES) and CC3/aug-cc-pVQZ (PS) levels, using the CFOUR code[2] and the VSCF/VCI Raman spectra were evaluated by the VSCFR code, developed by our group. Sample results are given in **Tables 1** and **2** below, which show the Raman shifts and differential cross sections of water. Those data were obtained using a 514.5 nm excitation wavelength with the usual 90° illumination-observation geometry, based on linearly polarized incident radiation and unpolarized recorded radiation. Sample's temperature is 400 K. The VSCF and VCI wave functions were obtained using a numeric representation of the PES, taken from reference [3]. Average percent difference between calculated and experimental data is also given in those tables ($\Delta\%$ column). Regarding the Raman shifts of the fundamental transitions (**Table 1**), they are clearly improved when one goes from the Harmonic model to the full-CI results (VCI[3]). On the other hand, the same behavior is not observed for the corresponding Raman intensities (**Table 2**), expressed as differential cross sections, particularly for the intensity of the asymmetrical O-H stretching vibration. In addition, while $\Delta\%$ for the Harmonic intensities is about 7%, the VCI[3] intensities have $\Delta\%$ equal to 19%. Despite the large uncertainties that accompany measured cross sections, the harmonic data are in better agreement with the experiment. As shown in **Table 1**, the VCI[3] wave functions seems to be very accurate. Therefore,

a numeric description of the PS, based on a tridimensional Gauss-Hermite quadrature, was adopted to investigate the accuracy of the second order Taylor representation of the PS. Due to the large number of electronic structure polarizability calculations required in such representation of the PS (thousands of points), the corresponding dynamic polarizabilities were evaluated at the CC3/aug-cc-pVTZ level. The cross sections obtained from the numeric representation of the PS were compared to the corresponding data from the Taylor representation (not show here). The observed differences between them were small (order of $10^{-37} \text{ m}^2 \text{ sr}^{-1}$). Currently, we are performing CC3/aug-cc-pV5Z calculations of the PS (Taylor representation), including additive corrections for the core-correlation effects at the CC3/aug-p(C)VQZ level, to further improve the PS towards the complete basis set limit. Also, vibrational corrections to the transition polarizability (see ref.[4]) will be included in order to assess if such disagreement, observed for the anharmonic intensities, are related to some limitation of the Placzek's model.

Table 1: Raman shifts (in cm^{-1}) for the fundamental transitions of ${}^1\text{H}_2{}^{16}\text{O}$ molecule.

	$v_1(a_1)$	$v_2(a_1)$	$v_3(b_2)$	$\Delta\%$
HARM	3831.1	1650.1	3940.7	4.6
VSCF	3714.0	1589.7	3889.0	2.2
VCI[3]	3657.3	1595.5	3756.1	0.0
Exp.[3]	3657.1	1594.7	3755.93	

Table 2: Differential cross sections (in $10^{-35} \text{ m}^2 \text{ sr}^{-1}$) for the fundamental transitions of ${}^1\text{H}_2{}^{16}\text{O}$.

	$v_1(a_1)$	$v_2(a_1)$	$v_3(b_2)$	$\Delta\%$
HARM	10.67	0.30	2.39	7.2
VSCF	12.00	0.38	2.61	14.2
VCI[3]	12.40	0.35	2.88	19.0
Exp.[5]	11.0 ± 1.2	0.33 ± 0.08	1.8 ± 0.2	

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Theoretical simulations for the Delta variant of SARS-CoV-2 for understanding the evolution of structural stability

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Keywords: SARS-CoV-2, Delta variant, molecular dynamics

1. Introduction

Currently, the most concern variant of SARS-CoV-2 is B.1.617.2 (Delta). It was associated with a rapid surge in cases in India, with evidence for increase in viral transmissibility. However, we do not know the molecular causes of this behavior. Thus, we initially sought to calculate the stability of the main mutations that constitute the Delta variant. In addition, we performed a quantitative/qualitative analysis on antibody-antigen chemical interactions.

2. Methodology

We performed a prediction of stability/affinity energy (kcal/mol) as a function of Delta variant mutations, using the Prime algorithm integrated with the Schrödinger Maestro 2021-2 software. For this, using the "Residue Scanning" module [1], all mutations were inserted computationally in the ACE2-Spike complex (PDB ID: 7DF4). In addition, we are currently simulating by molecular dynamics the mutations of the Delta variant with GROMACS 2019.1 software over 50 ns with 2 fs time step.

3. Results and Discussion

First of all, it should be noted that the negative sign in the results represents an increase in stability and affinity values (see Table 1). The T478K mutation resulted in a destabilization of +19.490 kcal/mol, while L452R achieved much higher stability at -8.161 kcal/mol. In terms of affinity T478K induced an increase in affinity in -5.046 kcal/mol while L452R in -0.182 kcal/mol. Consequently, a possible new variant would be one that has a slightly higher stability than those that already exist today. This is because the evolutionary trajectory of SARS-CoV-2 has been tending to a marginal stability, instead of the maximized value for which we obtained in the ACE2-RBD interaction at -96.252 kcal/mol. The marginal stability value in the literature [2] is at most -10 kcal/mol, and we note that viral evolution has been tending precisely to this value. According to quantitative analysis in Schrödinger Maestro 2021-2 software and qualitative analysis in DynaMut2 (see Figure 1), we noticed that the structure absent mutations, position L452 generated 2 (two) interactions with the neutralizing antibody COVOX-

278: Ile102 at a distance of 2.3 Å and Leu103 at 2.6 Å. On the other hand, when we had the structure containing the L452R mutation, all these interactions were lost.

Table 1: Stability results in the face of mutations that affected the Spike region of the Delta variant.

Mutation	Δ Affinity	Δ Stability	Δ Energy
T19R	0.000	+1.100	-68.740
L452R	-0.182	-8.161	-108.661
T478K	-5.046	+19.490	+17.150
D614G	0.000	-5.740	+97.340
D950N	0.000	-4.655	-15.815

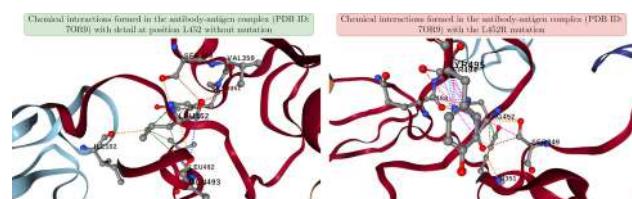


Figure 1: Chemical interactions formed as a result of the T478K and L452R mutations.

Conclusions

Therefore, the Delta variant has a worrying mutation, L452R, for inducing a high structural stability in ACE2-Spike. Finally, the virus has been seeking marginal stability reflecting a gradual evolution. However, it is very difficult from these results alone to predict with accuracy the behavior of the virus, and further in-vitro and in-vivo studies are required to confirm these findings.

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Uso de Ferramentas de Análise Bayseiana e de Redes Neurais Artificiais para Auxiliar na Determinação Estrutural do Levomenol por meio de Deslocamentos Químicos de RMN de ^{13}C e ^1H calculados em nível DFT

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Palavras-Chave: Levomenol, DP4+, ANN-PRA.

Introdução

A combinação de métodos computacionais e dados experimentais de Ressonância Magnética Nuclear (RMN) tem se mostrado de grande valia para a atribuição de moléculas orgânicas.¹ Antigamente, apenas os parâmetros estatísticos mais simples eram utilizados para avaliar e validar a correlação entre os deslocamentos químicos (δ) calculados e experimental de ^1H e ^{13}C RMN, como por exemplo o erro absoluto médio (MAD) e erro quadrático médio (RMSD). Recentemente, o desenvolvimento de novas ferramentas intensificou o tema reassinalamento estrutural, principalmente no que diz respeito à resolução da configuração relativa das moléculas orgânicas, especialmente os produtos naturais.¹ Entre essas novas ferramentas, os mais relevantes são o DP4+, que utiliza uma análise bayseiana,² e o ANN-PRA, que realiza uma análise de reconhecimento de padrões a partir do uso de redes neurais artificiais.³ De acordo com o nosso interesse na aplicação destas novas metodologias para a analisar estruturas de produtos naturais, neste estudo de caso, pretendemos mostrar as vantagens do uso complementar de DP4+² e ANN-PRA³ na diferenciação do levomenol, também conhecido como (-)- α -bisabolol (α -Bis), e seu epímero (+)-epi- α -bisabolol (epi- α -Bis), ver figura 1.

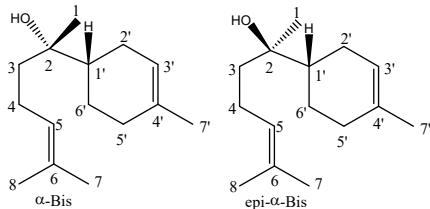


Figura 1. Estrutura do α -Bis e epi- α -Bis.

Resultados e Discussão

Os cálculos de deslocamento químico de RMN de ^1H e ^{13}C para o α -Bis e epi- α -Bis, realizados através da teoria do Funcional da Densidade acoplado ao método GIAO (GIAO-HDFT), em nível de teoria GIAO/mPW1PW91/6-31G(d)/mPW1PW91/6-31G(d) utilizando o pacote de software Gaussian 09³, forneceram valores de MAD e RMSD muito

semelhantes. α -Bis: 0,09 e 0,10 (RMN de ^1H) e 2,19 e 2,76 (RMN de ^{13}C), respectivamente. Para o epi- α Bis: 0,15 e 0,19 (RMN de ^1H) e 2,29 e 2,69 (RMN de ^{13}C), respectivamente. Esses valores muito similares impossibilitam uma discriminação inequívoca sobre a real identidade do produto natural isolado. No entanto, ao aplicar as novas ferramentas, DP4+ e Ann-Pra, o cenário mudou drasticamente. Com o DP4+ existe uma clara indicação do α -Bis como sendo a molécula isolada e identificada experimentalmente, ver figura 2. A ferramenta ANN-PRA, por sua vez, confirmou essa análise apontando o α -Bis como estrutura correta.

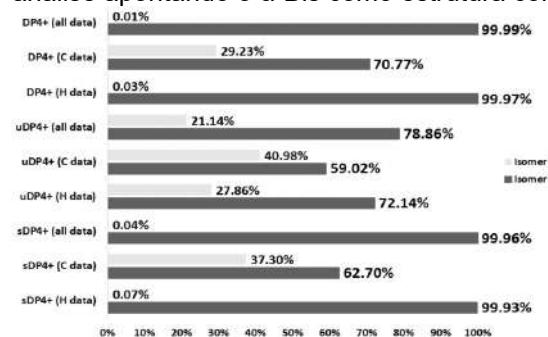


Figura 2 Valores do DP4+ para o α -Bis (isomer 1) e para o epi- α -Bis (isomer 2).

Conclusão

Embora não seja possível descriminar a estrutura do α -Bis e seu epímero epi- α -Bis baseado apenas nos descritores MAD e RMSD, as análises realizadas utilizando as novas ferramentas, DP4+ e ANN-PRA, confirmaram que o produto natural isolado é o α -Bis

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Solvatochromic reversal in a merocyanine under an oriented external electric field.

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Keywords: merocyanine, solvatochromism, DFT

1. Introduction

Spiropyrans (SP) are photochromes which reversibly photoisomerize to highly conjugated open form named merocyanines (MC) (**Figure 1**).

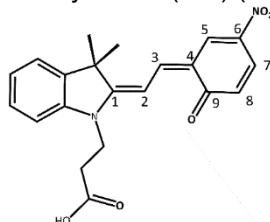


Figure 1. Transoid MC isomer structure.

In this study the solvatochromic behavior of the MC will be investigated. Usually, this behavior consists in negative or positive solvatochromism. However, some dyes present a solvatochromic reversal, a process where the solvatochromic behavior changes from positive to negative¹. To investigate the possibility of this reversal in the MC an electrostatic field was used to mimic the solvent environment around the molecule.

2. Methodology

An external electrostatic field parallel to the MC electric dipole was used to distort the geometry and provoke electronic effects. The intensity of the field was varied from zero to 200×10^{-4} a.u within intervals of 5×10^{-4} a.u. DFT calculations at each field intensity were carried out using the CAM-B3LYP functional and the 6-31G(d,p) basis set. To separately evaluate the influences of both structural and electronic changes three distinct calculation setups according to the proposal of Manzoni and co-workers²:

1) Flexible geometry/no Field (FG/nF): The geometry is optimized in the presence of the electrostatic field, then, all properties are calculated after removing the field and keeping the field-distorted geometry.

2) Rigid geometry/with Field (RG(X)/wF): The geometry is kept fixed at the gas phase structure (X=n) or at the fully distorted optimized geometry at field intensity of 200×10^{-4} a.u (X = z). The electric field at given intensity is then applied to the system in order to perform the calculation of the electronic properties.

3) Flexible geometry/with Field (FG/wF): Both geometry and electronic properties are computed in the presence of the electrostatic field.

3. Results

In **Figure 2** the calculated absorptions energies for the HOMO→LUMO transitions in function of the electrostatic field intensity are presented.

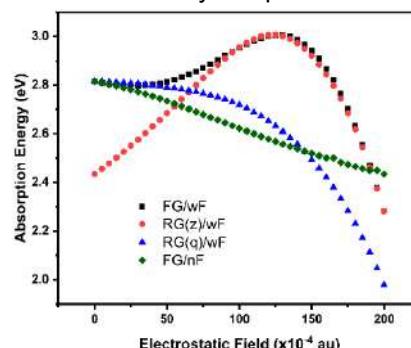


Figure 2. Theoretical calculated absorption spectrum of the MC as function of the applied electrostatic field.

Considering electronic and geometric effects (FG/wF), the absorption energies are in agreement with the RG(q)/wF results until the intensity of the electrostatic field reaches $E = 40 \times 10^{-4}$ a.u. Which means that by this point the structure starts to assume a zwitterionic character. Then, when the field intensity reaches $E = 85 \times 10^{-4}$ a.u the FG/wF setup starts to present the same results as the obtained in the RG(z)/wF further confirming the structural change.

4. Conclusions

Through the usage of an unexpensive methodology a solvatochromic reversal was detected for the MC molecule which depends both on geometry distortion and electronic effects.

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Photostability of Vitamin C: Surface Hopping Dynamics and intramolecular load transfer analysis.

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Palavras-Chave: Surface Hopping Dynamics, Vitamin C, Photobiochemistry.

Vitamin C is an essential nutrient for humans, being important in several biochemical, photochemical and antioxidant activities.^{1,2} However, many mechanisms of vitamin C activity are not yet fully understood, such as, for example, an intramolecular charge transfer, photochemical stability and the time decay of their excited states. In this sense, the present work had as main objective the analysis of the first 12 excited states of vitamin C, classifying them in local excitations, charge transfer or Rydberg states. In addition, the decay time for each excited state was estimated using the Surface Hopping molecular dynamics (DMSH). In DMSH, the Khon-Sham orbitals were expanded using flat waves with 75 Ry cut-off, PBE exchange and correlation functional and Troullier-Martins of conserved norm pseudopotential. The temperature was controlled at 300 K using a chain of three Nosé-Hoover thermostats. The UV-vis spectra were chosen using TD-DFT with the CAM-B3LYP, B3LYP and PBE exchange and correlation functionals and the 6-31G base set.³ The effect of the aqueous solvation was included in the calculations explicitly and implicitly. The results of the calculations show that the geometric parameters obtained theoretically have good agreement with the experimental values. It is also observed that the λ_{max} obtained with the implicit and explicit inclusion of the aqueous solvent was 246.40 nm and 245.43 nm, respectively. These results when compared with the λ_{max} in gas phase represent a displacement of 21.5 and 20.53 nm, respectively. In 33,33 % of the analyzed excited states, charge transfer occurs, and the excitations are predominantly of the type $\pi \rightarrow \pi^*$.

Of all the DMSH trajectories analyzed, photodegradation was not observed, that is, vitamin C shows photochemical stability, which makes it possible, for example, to use this molecule in photoelectric devices and sunscreens.⁴

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Estudo teórico de formação de prata metálica do $\beta\text{-Ag}_2\text{WO}_4$ induzida por irradiação de elétrons

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Palavras-Chave: Nanopartículas de prata; difusão; feixe de elétrons; dinâmica molecular ab initio.

INTRODUÇÃO

Há alguns anos, foi observado a nucleação e o crescimento de nanocrystalas de prata metálica nas superfícies do $\alpha\text{-Ag}_2\text{WO}_4$ após a irradiação de elétrons induzida por feixes de elétrons provenientes de microscópios eletrônicos *in situ*¹ e também por técnicas de laser em femtosegundo. Esses experimentos produziram um grande interesse no que diz respeito à interação elétron/materia que leva à formação de nanoestruturas metálicas a partir de um nível atômico fundamental. Portanto, este trabalho tem como objetivo estudar os passos iniciais que induzem a formação dessas nanoestruturas metálicas sobre as superfícies da fase metaestável do $\beta\text{-Ag}_2\text{WO}_4$.

METODOLOGIA

Cálculos de química quântica baseada na DFT com condições periódicas de contorno foram efetuados como implementado no pacote VASP. Ondas planas foram utilizadas na descrição dos orbitais de Kohn-Sham. Os efeitos dos elétrons internos foram tratados com o método PAW. O grid de k -points $3 \times 3 \times 1$ foi utilizado para todas as superfícies. O estudo dos processos de difusão atômica dos átomos Ag foram investigados pelo método NEB. E os aspectos relacionados à dinâmica de difusão dos átomos no interior do semicondutor foram estudados por meio da dinâmica molecular ab initio (DMA).

RESULTADOS

Em estudos teóricos anteriores, os estágios iniciais referentes ao crescimento de prata metálica no $\alpha\text{-Ag}_2\text{WO}_4$ foram investigados e mostraram que os mecanismos de difusão de cátions de prata envolvem barreiras de energia inferiores a 0,1 eV². No entanto, nossos estudos em superfícies $\beta\text{-Ag}_2\text{WO}_4$ indicam barreiras superiores a 0,4 eV, juntamente com a formação de dímeros e trímeros de prata em regiões internas às superfícies. Esses resultados sugerem mecanismos diferentes nas fases iniciais do crescimento metálico. A exemplo a figura 1, evidencia a formação de aglomerados metálicos internos à superfície (001).

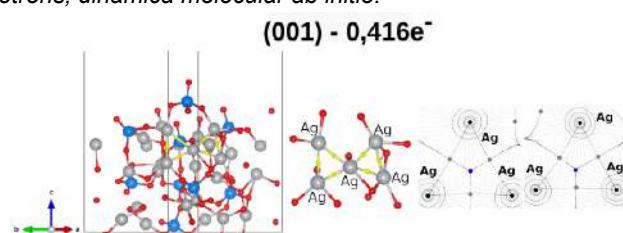


Figura 1: Representação dos aglomerados de Ag formados na superfície (001) do $\beta\text{-Ag}_2\text{WO}_4$ a 0,416 e $^-$ / $\beta\text{-Ag}_2\text{WO}_4$.

Uma análise da topologia de carga dos aglomerados formados mostra valores da ordem de 2,67 para o laplaciano da densidade enquanto o *bulk* de prata possui 1,59 para a mesma propriedade, confirmando a natureza metálica dos aglomerados.

CONCLUSÕES

Os resultados indicam que as superfícies do $\beta\text{-Ag}_2\text{WO}_4$ apresentam uma rápida formação de prata metálica no interior das superfícies, embora a barreira energética seja superior ao do $\alpha\text{-Ag}_2\text{WO}_4$. No entanto, devido a perda de simetria nas superfícies essa barreira energética é rapidamente transposta. Ademais, os resultados referentes a topologia de densidade de carga mostram valores equivalentes a prata metálica.

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AGRADECIMENTOS

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Análise quimiométrica de seletividade nos sítios ativos de cisteíno proteases da família da papaína para o estudo de substâncias antiparasitárias e antineoplásicas.

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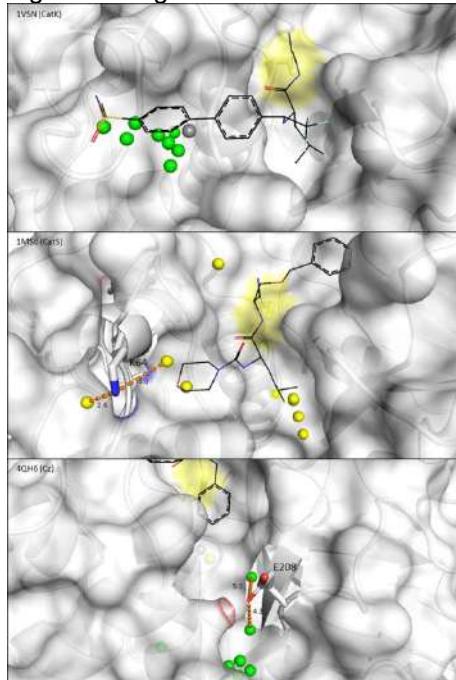
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Palavras-Chave: quimioinformática, planejamento baseado na estrutura, campos de interação molecular (MIF).

Introdução

Cisteíno Proteases estão envolvidas em diversos processos fisiopatológicos nos seres humanos. As enzimas deste trabalho pertencem à família da Papaína e são alvos terapêuticos para diversas patologias: cruzaina do protozoário *Trypanosoma cruzi* (doença de chagas) e catepsinas humanas: B, L e S (câncer) e K (osteoporose). A alta similaridade no sítio ativo destas enzimas faz com que o planejamento de inibidores seletivos se torne um desafio.¹ Os sítios ativos das proteínas foram mapeados energeticamente por meio dos Campos de Interação Molecular utilizando-se sondas *in silico*. Os dados obtidos foram utilizados em uma Análise de Componentes Principais que destacou regiões de seletividade para 3 destas enzimas: Catepsinas K, S e cruzaina (Figura 1), racionalizando desta forma a busca por grupos químicos em dipeptidil nitrilas presentes no banco de dados ChEMBL.

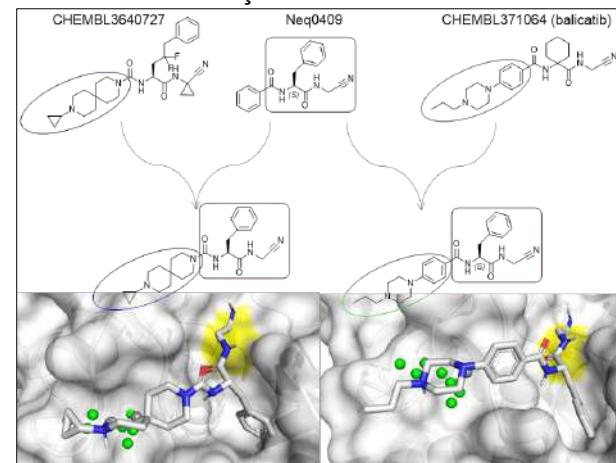
Figura 1–Regiões de seletividade nos sítios ativos.



Legenda: esferas verdes representam o íon sódio, enquanto as amarelas representam o íon cloreto.

As moléculas selecionadas serviram como blocos construtores para o planejamento de novos inibidores dipeptidil nitrila que foram docados, com os candidatos mais promissores obtidos a partir da hibridização molecular (técnica em planejamento baseado no ligante) com a molécula *in house* Neq0409. Híbridos moleculares (Figura 2) foram planejados com potencial inibidor da catepsina K e estão sendo sintetizados para a avaliação da atividade biológica.

Figura 2 – Novas dipeptidil nitrilas com potencial inibitório da catepsina K planejadas a partir da técnica de hibridização molecular.



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Cálculos de frequências vibracionais em moléculas diatômicas usando os modelos de osciladores harmônico e anarmônico

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Palavras-Chave: Oscilador Harmônico, Anarmonicidade, Moléculas Diatômicas.

INTRODUÇÃO: Cálculos de estruturas eletrônica e molecular têm se tornado rotineiros no estudo de sistemas moleculares diversos. Há uma grande variedade de métodos disponíveis para o estudo de propriedades como: comprimentos de ligação, análises de espectros de infravermelho, energias de ligação, momentos de dipolo, espectros UV-Vis, entre outras. Os dois principais grupos são os métodos *ab initio* e da teoria do funcional de densidade. No entanto, a descrição apropriada dos espectros de IV vai além dessas abordagens teóricas, sendo também função da descrição do modelo de oscilação, harmônica ou anarmônica. Para avaliar essa característica, nesse trabalho estudou-se um conjunto de moléculas diatômicas (HF, F₂, HCl, Cl₂, N₂, O₂, KF, CaO, NaF e NaCl) considerando-se os modelos de osciladores harmônico e anarmônico.¹

METODOLOGIA: Para uma análise comparativa dos cálculos de comprimento de ligação de equilíbrio e frequência vibracionais, considerando-se comportamentos harmônico e anarmônico, empregou-se os métodos *ab initio*: HF, MP2, CISD, CCSD(T) e de funcionais da densidade: B3LYP, wB97XD, M08HX, PBE0. A função de base utilizada em todos os cálculos foi aug-cc-pVTZ. O comportamento de oscilador harmônico foi avaliado através da otimização completa e cálculos diretos de frequências vibracionais. Já o estudo anarmônico foi feito considerando-se cálculos *single point* de energia variando-se o comprimento de ligação – Eq. (1)

$$E(R) = \frac{1}{R} \sum_{k=0}^5 C_k (R - R_e)^k \quad (1)$$

A constante de força associada à ligação química é dada pela Eq. (2), e consequentemente a frequência vibracional no modelo anarmônico, pela Eq. (3)

$$K = \left(\frac{\partial^2 E(R)}{\partial R^2} \right)_{R=R_e} \quad (2)$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \quad (3)$$

Os dados obtidos foram comparados com os resultados experimentais e análise estatística usando o RMSD (*Root-Mean-Square Deviation*). Todos os cálculos foram feitos com o programa Gaussian16.

RESULTADOS:

Na Tabela 1 estão sumarizados, a título de ilustração, os resultados de RMSD apenas para os métodos MP2, CCSD(T), B3LYP e PBE0, tanto para o oscilador harmônico como anarmônico (os resultados completos serão apresentados no evento).

Tabela 1: Comparação de RMSD

MOLÉCULAS	MP2	CCSD(T)	B3LYP	PBE0	Exper
HF	3327.6436 (4123.0505)	3327.4232 (4126.93692)	3326. (4072.3597)	3327.3772 (4143.4387)	4138.32
F ₂	937.4090 (1003.2869)	936.9981 (915.5683)	937.1883 (1052.9322)	937.0922 (1104.2702)	916.64
HCl	3026.8643 (3044.9060)	479.7475 (2990.9284)	3029.5779 (2942.3147)	3026.8643 (2993.0482)	2990.946
Cl ₂	480.2415 (572.7949)	479.9475 (541.7464)	467.4815 (538.8610)	484.4251 (576.2236)	559.7
N ₂	1197.3681 (2186.8645)	1343.8247 (2340.3668)	1197.2021 (2447.2157)	1197.4477 (2478.9321)	2358.57
O ₂ (triplet)	1092.5175 (1454.6582)	1152.2650 (1574.6263)	1092.9890 (1614.6667)	1092.6139 (1691.9978)	1580.19
KF	478.7560 (455.8601)	483.4161 (455.6704)	250.0341 (469.2697)	517.6549 (471.4145)	428.
CaO	680.4140 (644.9491)	675.3204 (754.6935)	690.8715 (799.5948)	691.2583 (825.4748)	732.1
NaF	628.0609 (524.0614)	633.4490 (531.3620)	625.4653 (523.0491)	630.1037 (525.8498)	536
NaCl	380.2663 (346.8214)	376.9183 (346.8819)	381.6952 (354.5439)	424.1762 (357.4693)	366
RMSD	475.9592 (80.5895)	435.2506 (15.7432)	479.3792 (64.9989)	476.7477 (87.2825)	ANARMÔNICO HARMÔNICO

NOTA: Valores apresentados fora do parêntese se referem ao modelo Anarmônico.

Valores apresentados dentro do parêntese referem-se ao Harmônico

Nota-se pelos valores de RMSD que o modelo anarmônico é o que melhor se ajusta à descrição experimental em tais sistemas químicos (moléculas diatômicas), enquanto as frequências vibracionais harmônicas são uma boa aproximação.

CONCLUSÕES:

O estudo de propriedades eletrônicas em sistemas moleculares, além da metodologia usada, também é dependente do modo correto da descrição de tais propriedades. No caso de moléculas diatômicas, a descrição das frequências vibracionais é possível de ser feita usando o modelo de oscilador anarmônico usando-se para isso uma função potencial. Observa-se pelos resultados de RMSD que esse modelo é o que melhor se ajusta aos dados experimentais. Trabalho envolvendo fluoretos e óxidos de lantanídeos está em andamento.

AGRADECIMENTOS: IQ/Unicamp, FAPESP e CNPq.

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Describing the spectra and electronic structure of the Si⁺ monocation

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Palavras-Chave: *sulfur monoiodide cation, electronic states, spin-orbit coupling*

Introduction

Over the last years, the role played by molecular systems containing sulfur and halogens, such as SX_2 , S_2X ($\text{X} = \text{F}$, Cl , and Br) on atmospheric chemistry and plasma etching processes has been well established¹⁻³. Experimental and theoretical studies on the neutral diatomic molecules, SX ($\text{X} = \text{F}$, Cl , Br , and I), are scarce, in contrast with the isovalent diatomics oxygen-halogen, known to play important roles as reservoirs of halogen radicals in the Earth's upper atmosphere. Our group has carried out theoretical investigations on the heavier systems SBr and SrI , motivated by their possible formation in regions of strong volcanic activity, then contributing to the description of their energetic profile and discovering potential difficulties in their experimental investigation. Hence, the present work emerges as a natural extension of our previous studies on neutral diatomics. Although theoretical studies are unknown, experimentally, the SI^+ molecule was detected by Fletcher et al.^{4,5} through the dissociation of the short-lived complex $[\text{ICS}_2]^{2+}$, a product of the reaction of I^{2+} with CS_2 , and also in the collision of I^{3+} with SO_2 . This study aims to report a detailed characterization of the low-lying relativistic states of SI^+ employing highly correlated ab initio methods, and compute the associated spectroscopic parameters transition probabilities, and dipole moment functions.

Methods

In the first step, the eighteen A+S electronic states correlated with the two lowest-lying dissociation channels, namely $S^+(^4S_u) + I(^2P_u)$ and $S(^3P_g) + I(^3P_g)$, were calculated in a SA-CASSCF calculation. For that, 10 electrons were excited into an active space including the 3s, 3p, and 4s orbitals of sulfur and the 5p orbital of iodine. The next step accounted for dynamical correlation effects using an icMRCI calculation on top of the CASSCF reference wavefunction. The aug-cc-pV(5+d)Z basis functions were used for sulfur and the aug-cc-pV5Z-PP for iodine. Relativistic effects were included by evaluating the spin-orbit matrix elements at the CASSCF/av5z level and replacing the diagonal elements of the spin-orbit matrix with the correlated MRCI energies as implemented in Molpro suite of programs.⁶

Acknowledgements

The authors would like to thank CNPq and FAPESP for all the support in this work.

Results

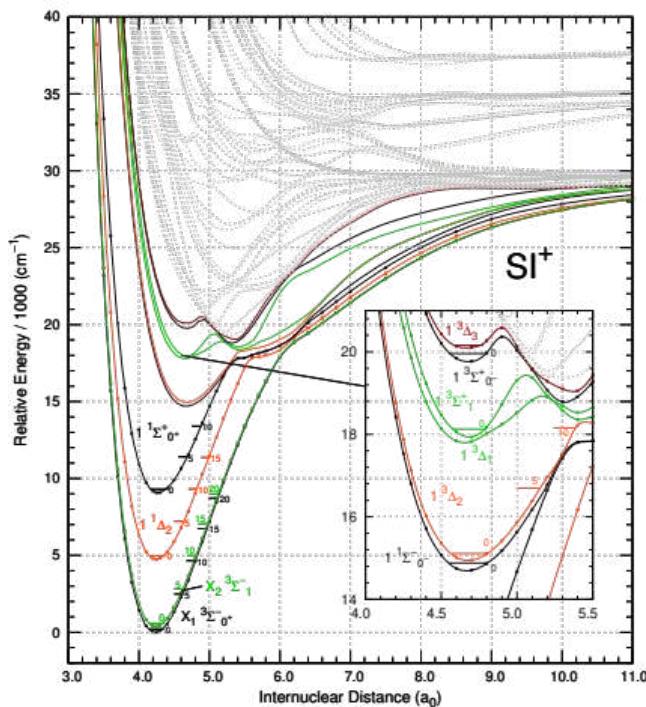


Fig 1 – Potential energy curves of the lowest-lying Ω states of SI^+ .

Conclusions

A complete characterization of the electronic states of the ion SI^+ is reported for the first time in the literature. Once the lowest-lying dissociation channels correspond to sulfur atom ionization and the other to iodine atom ionization, the energetic profile of SI^+ differs from that of SF^+ and SCI^+ . A dense and complex structure of states containing several avoided crossings is revealed for energies above $\sim 17000 \text{ cm}^{-1}$. The spectroscopic parameters, transition probabilities, and a simulation of the ionization process $\text{SI}^+ + \text{e}^- \rightarrow \text{SI}$ were obtained.

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Efeitos da flexibilidade conformacional e da anarmonicidade torcional na distribuição dos produtos da reação 2-butanona + H

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Palavras-Chave: flexibilidade conformacional, anarmonicidade torcional, cinética.

Introdução

Como forma de redução da emissão gases do efeito estufa, é crescente a busca por alternativas utilizando combustíveis à base de biomassa, que podem ser capazes de substituir ou serem misturados aos combustíveis fósseis. A 2-butanona surge como potencial candidata a biocombustível devido ao seu grau de octanagem (RON = 117) e sua capacidade de ser utilizada como *fuel tracer*, devido a sua habilidade a fluorescência^[1,2].

As reações de abstração de hidrogênio deste composto são responsáveis pelo início do processo de oxidação^[1,3], levando a formação de três produtos radicalares mais o gás hidrogênio: 2-butanona-1-il + H₂ (**R1**), 2-butanona-3-il + H₂ (**R2**) e 2-butanona-4-il + H₂ (**R3**), em diferentes proporções. Dentro desse contexto, este trabalho tem como objetivo analisar a variação dos modelos cinéticos na distribuição destes produtos, numa ampla faixa de temperaturas.

Metodologia

As distribuições dos diferentes produtos das reações deste estudo, foram obtidas através de simulações cinéticas de Monte Carlo, empregando as constantes de velocidade obtidas pelas aproximações baseadas na teoria do estado de transição, *one-well* (1W), *multistructural* (MS) e *multipath* (MP), com a inclusão do tunelamento multidimensional de pequena curvatura (*Small-Curvature Tunneling* – SCT), calculadas numa faixa temperaturas de 250 a 2500 K. A anarmonicidade associada aos modos vibracionais de torção foi introduzida através das funções de partição rotacionais-vibracionais, utilizando o modelo *Multi-Structural Method with Torcional Anharmonicity Based on a Coupled torcional Potential* - MS-T(C). As informações dos pontos estacionários gerados pela reação proposta foram obtidas no nível de teoria M06-2x/6-31+G(d,p), utilizando o GAUSSIAN 09. As constantes de velocidade térmica e a distribuição dos produtos foram estimadas através do PILGRIM v2020.1. As funções de partição foram calculadas pelo código MsTor.

Resultados e Discussão

As distribuições dos produtos da reação proposta são mostradas na **Figura 1**. É possível notar que a

ocorrência dos produtos de (**R1**), a formação da 2-butanona-1-il + H₂, é favorecida quando múltiplos caminhos e a anarmonicidade torcional é considerada [MP-CVT/SCT(Anh.)]. A comparação entre os valores da distribuição dos produtos para as estimativas MP-CVT/SCT(Har.) e MP-CVT/SCT(Anh.) indicam que a inclusão da anarmonicidade torcional diminui a formação dos produtos de (**R3**), ou seja, 2-butanona-4-il + H₂. Para (**R2**), nossos resultados mostram que não a inclusão de efeitos dinâmicos e não-dinâmicos, de múltiplos caminhos reacionais e, da anarmonicidade torcional (1W-TST), superestimam a formação de 2-butanona-3-il + H₂, uma vez que essas constantes de velocidade estão superestimadas.

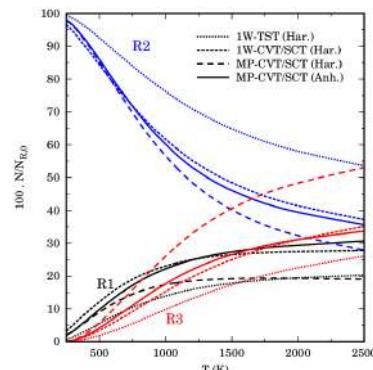


Figura 1. Distribuições dos produtos obtidas por diferentes modelos cinéticos.

Conclusão

Neste estudo, verificamos que a estimativa da distribuição dos produtos da reação da 2-butanona com hidrogênio atômico é fortemente influenciada pelos efeitos dinâmicos, pela inclusão da anarmonicidade torcional, e pela de múltiplas estruturas de reagentes e estados de transição.

Agradecimentos

Os autores agradecem o apoio financeiro do CNPq e CAPES.

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Abordagem teórica para a dispersão rotatória óptica

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Palavras-Chave: ORD, RMSD, moléculas quirais.

Introdução

A dispersão rotatória óptica (ORD, do inglês *optical rotatory dispersion*), propriedade quiral bastante explorada, pode auxiliar na elucidação estrutural ou na identificação enantiomérica de uma amostra. O cálculo teórico da ORD pode corroborar com dados experimentais. Este estudo faz uma comparação metodológica no cálculo de ORD de um conjunto de 44 moléculas quirais rígidas (Fig. 1) com valores experimentais disponíveis.

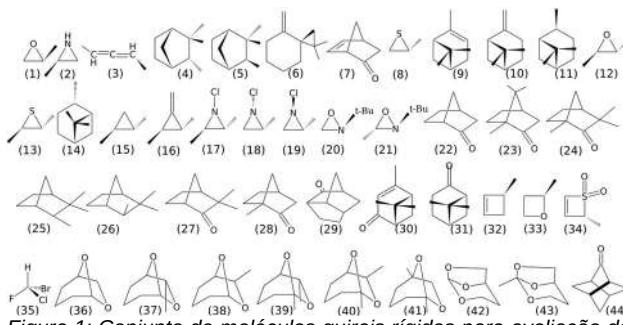


Figura 1: Conjunto de moléculas quirais rígidas para avaliação de dispersão rotatória óptica (ORD).

Metodologia

As moléculas 1-14 foram estudadas nos níveis Hartree-Fock (HF) e funcional de densidade (B3LYP, CAM-B3LYP, PBE0, wB97X-D, M06-2X) e conjuntos de base aug-cc-pVDZ, aug-cc-pVTZ, 6-311G++(2d,p) e 6-311G++(3df,2p). Os resultados foram comparados com valores experimentais disponíveis^[1] e fez-se uma análise hierárquica de clusters para agrupamento dos dados por similaridade. As moléculas 7-44 foram comparadas em relação aos valores experimentais^[2] usando funcionais CAM-B3LYP, PBE0 e wB97X-D e mesmos conjuntos de base. A ORD também foi calculada nas condições CAM-B3LYP/3-21G e HF/aug-cc-pVTZ. Os cálculos de otimização de geometria e ORD foram realizados com o programa Gaussian 16.^[3]

Resultados

A primeira comparação com valores experimentais foi expressa na forma de RMSD, raiz do desvio médio quadrático, para os valores normalizados, como mostra a Fig. 2. Uma análise hierárquica de clusters mostra o agrupamento por similaridade dos resultados (Fig. 3), corroborando com os valores obtidos. Os desvios dos resultados para as moléculas 7-44 nos 3 funcionais escolhidos podem ser vistos na Fig. 4, além de um teste da eficiência do CAM-B3LYP com uma base inferior, assim como o nível HF com a base com melhores resultados no estudo inicial.

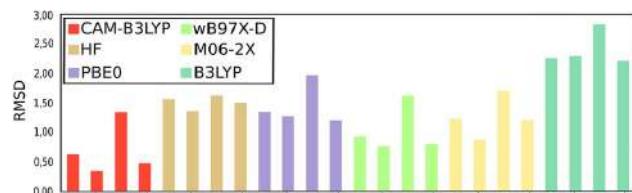


Figura 2: RMSD para valores normalizados de dispersão rotatória óptica das 14 moléculas quirais abordadas no estudo sob diferentes metodologias. a) aug-cc-pVDZ, b) aug-cc-pVTZ, c) 6-311++G(2d,p) e d) 6-311++G(3df,2p)

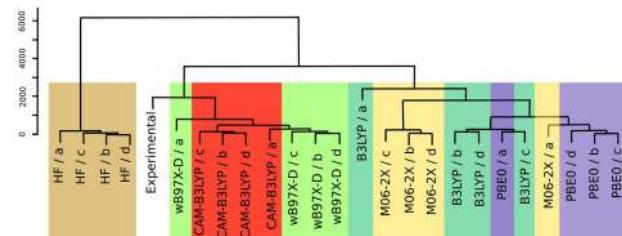


Figura 3: Análise hierárquica de clusters para metodologias teóricas e valores experimentais de OR para moléculas 11-14. a) aug-cc-pVDZ, b) aug-cc-pVTZ, c) 6-311++G(2d,p) e d) 6-311++G(3df,2p)

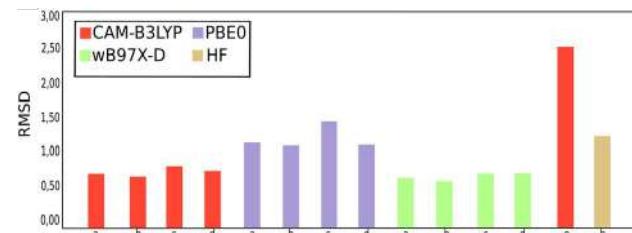


Figura 4: RMSD para valores normalizados de dispersão rotatória óptica das moléculas 7-44 com diferentes funcionais e funções de base. a) aug-cc-pVTZ, b) 6-311++G(2d,p), c) 6-311++G(3df,2p) e e) 3-21G

Conclusão

Os funcionais CAM-B3LYP e wB97X-D apresentaram os melhores desempenhos, destacando-se as funções de base aug-cc-pVTZ e 6-311++G(3df,2p). Seus resultados se assemelham entre si e com os dados experimentais, e se mostram promissores.

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Agradecimentos





IN SILICO PROSPECTING INHIBITORS GLUTAREDOXIN A1 OF CORYNEBACTERIUM PSEUDOTUBERCULOSIS

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Keywords: Homology Modeling, Molecular Dynamics, Virtual Screening.

INTRODUCTION

Caseous lymphadenitis (CL) is an infectious disease caused by the pathogenic microorganism *Corynebacterium pseudotuberculosis* (Cp) and causes great economic losses in livestock farming worldwide. The absence of effective therapies against the pathogen opens the way for the investigation of possible drug candidates. The generation of oxidative stress in bacteria makes it difficult to reproduce and can lead to death¹. The Cp bacteria produce the protein Glutaredoxin A1 (Cp-GrxA1), which functions as a reduction buffer against Reactive Oxygen Species (ROS). In this context, when understanding the aspects of bacterial defenses, *in silico* approaches can assist in inhibition strategies of this mechanism. In summary, the present work aims to search for possible inhibitors of the GrxA1 protein of *C. pseudotuberculosis*, through computational simulations by Molecular Dynamics (DM) and Virtual Screening (VS). The results can lead us to understand the molecular docking between the aforementioned protein and selected compounds, to make a parallel with experimental data supporting the hypothesis of performing *in vitro* assays.

METHODS

Study method process

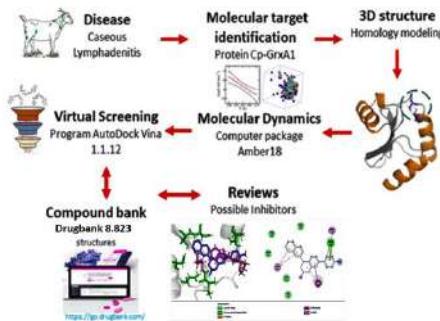


Figure 1: Workflow of the study

RESULTS

The three-dimensional structure of GrxA1 was constructed by homology in its active form and, in sequence, simulated for 200 ns with the DM technique.

In the second stage, using molecular docking and Virtual Screening, we found a total of 26 molecules with the potential inhibitor of GrxA1. The types of protein-ligand interactions for each molecule found were studied. Thus, we present the results for one of the structures found. Figure 2.

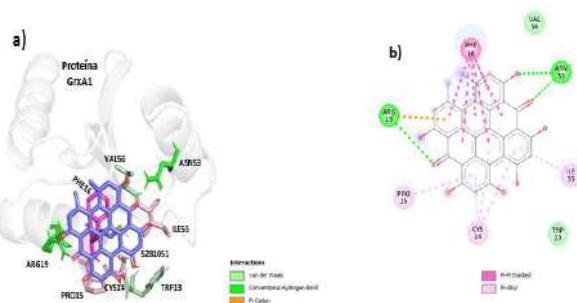


Figure 2: Representation of the interaction between the compound 5281051 and the GrxA1 protein. Figure a) in 3D and b) 2D, present the most relevant amino acids for the interaction, as well as the types of interactions.

CONCLUSION

We have identified a set of molecules that are being investigated, how much their ability to inhibit the Cp-GrxA1 protein. Although still in the preliminary phase, the study paves the way for the development of new medicines and biotechnological applications, contributing to assist in the treatment and/or cure of Caseous Lymphadenitis, thus generating great interest for this sector of the economy.

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XXI SBQT

Estudo do tautomerismo ceto-enólico da 7-*epi*-clusianona através de cálculos teóricos de deslocamentos químicos de RMN.

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Palavras-Chave: Tautomerismo, DFT, RMN.

Introdução

As atividades biológicas e farmacológicas de um produto natural estão diretamente ligadas às suas estruturas químicas. Assim, uma etapa crucial da análise das propriedades farmacológicas de um produto natural é a sua correta caracterização estrutural. Neste cenário, os cálculos teóricos de deslocamentos químicos têm desempenhado um papel eficaz e de baixo custo.¹ No presente trabalho, foi aplicado um protocolo de cálculos de deslocamentos químicos de ¹³C e ¹H a fim de estudar o tautomerismo da 7-*epi*-clusianona (figura 1).²

Metodologia

Para todos os cinco tautômeros possíveis da 7-*epi*-clusianona (figura 1), foi feita uma busca conformacional utilizando o método Monte Carlo com o campo de forças MMFF, no software Spartan '14. Das conformações encontradas, aquelas com energia relativa < 10 kcal.mol⁻¹ foram submetidas a cálculos de *single point* de energia, no nível de teoria B3LYP/6-31G(d). Na etapa seguinte, os confômeros com energia relativa < 5 kcal.mol⁻¹ passaram por uma otimização de geometria no nível mPW1PW91/6-31G(d). A partir desta etapa, foram selecionados os confômeros que apresentassem energia relativa de até 3 kcal.mol⁻¹. Com os confômeros restantes, foram realizados os cálculos de tensores de proteção magnética istrópica de ¹³C, utilizando o método GIAO, no nível mPW1PW91/6-31G(d). Todos os cálculos foram realizados utilizando o software Gaussian 09, em fase gás. Os tensores foram ponderados de acordo com sua distribuição conformacional, utilizando a equação de Boltzmann e transformados em deslocamentos químicos calculados, pela diferença com a molécula de referência (TMS). Ao final, os deslocamentos químicos calculados foram escalonados utilizando a equação linear $\delta_{\text{esc}} = 1,05\delta_{\text{calc}} - 1,22$.³

Resultados

A tabela 1 mostra os valores de desvio médio absoluto (MAD) e desvio médio quadrático (RMSD), obtidos a partir dos deslocamentos químicos calculados para os cinco possíveis tautômeros em fase gás e dos deslocamentos químicos experimentais dos tautômeros B e C, obtidos em solução de benzeno-d₆.²

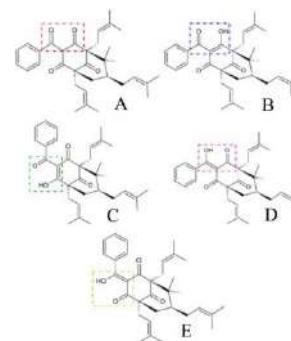


Figura 1: Representações estruturais dos tautômeros da 7-*epi*-clusianona.

Tabela 1: Valores MAD e RMSD (em ppm) dos deslocamentos químicos de ¹³C calculados em relação aos deslocamentos químicos experimentais dos tautômeros B e C.²

δ_{exp} (Tautômero B)	δ_{exp} (Tautômero C)				
	$\delta^{13}\text{C}_{\text{esc}}$ (ppm)	RMSD (ppm)	$\delta^{13}\text{C}_{\text{esc}}$ (ppm)	RMSD (ppm)	
A	5,86	9,42	A	5,46	9,19
B	2,26	2,71	B	2,76	3,29
C	2,73	3,23	C	2,94	3,41
D	3,53	4,23	D	3,92	5,03
E	3,06	3,85	E	3,04	3,75

Conclusões

A partir da análise de MAD e RMSD, obtidos entre os deslocamentos químicos calculados para os tautômeros A-E e os experimentais de B e C,² chegou-se à conclusão de que, em solução, estariam em equilíbrio os tautômeros B e C, como reportado por dos Santos e colaboradores.² Os resultados indicam a sensibilidade da metodologia em reconhecer as espécies em equilíbrio em uma solução de molécula que possua diversos tautômeros. Com o intuito de enriquecer a análise, avaliando se seria possível distinguir os deslocamentos químicos dos tautômeros B e C, são necessários cálculos utilizando modelos de solvatação.

Agradecimentos

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In the search of a reliable method to simulate the H₂S scavenging activity of aldehydes with DFT

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Keywords: DFT, H₂S scavenger, Reaction mechanism.

Introduction

Hydrogen sulfide is one of the major problems in the petroleum industry, promoting the fouling and corrosion of equipments. The most utilized non-regenerative scavengers are triazines-based molecules¹. In a previous work, we investigated thermodynamic and kinetics aspects related to the H₂S scavenging activity from the most representative triazine, being able to justify why only two equivalents of H₂S are consumed by each equivalent of scavenger¹. This class of scavenger, however, present some drawbacks, such as the ability to form heavy polymeric amorphous by-products throughout the production line².

In this context, alternative aldehyde-based scavengers have been gaining attention from the industrial and scientific community. However, due to the notorious carcinogenic reputation of formaldehyde, it has limited use in field applications. A possible solution is the *in situ* generation of formaldehyde with formaldehyde releaser compounds, such as hemiformals³.

Since few works simulate thermochemistry and kinetics related to H₂S sequester by aldehydes, in this work, we aim to understand how different aldehydes interact and react with H₂S acting as scavengers by simulating the energy change throughout the reaction steps and inspecting thermodynamic and kinetic parameters. Previous articles point out that, reaction path may occur without the bisulfide anion formation⁴. For the first step of our work, due to the lack of computational works concerning this topic, the goal is to validate a computational method based on the Density Functional Theory (DFT), according to energetic parameters, to further investigate the energy profile for the H₂S scavenging activity of aldehydes employed industrially.

Methods

For the computational method validation, we used the formaldehyde hydration reaction, considering implicit solvation using water, shown in Fig. 1. The following functionals, B3LYP; CAM-B3LYP; M06-2X; N12SX; OLYP; and ωB97X-D, combined with the 6-311+G(d,p); 6-311++G(d,p); aug-cc-pVDZ; aug-cc-pVTZ; and aug-cc-pVQZ basis sets, were tested. For the solvation simulation we used the integral equation formalism variant (IEFPCM). To choose the best computational method, we compared the simulated enthalpy change values of the hydration

reaction of formaldehyde with the experimental value ($\Delta H = -7.50 \text{ kcal mol}^{-1}$)⁵.

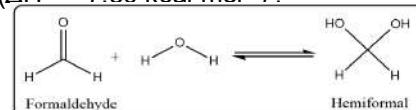


Fig. 1. Formaldehyde hydration reaction

Results

Fig. 2 shows that, among the evaluated functional and regardless of the assessed basis set, M06-2X functional yields the lowest values of absolute deviation compared to the reference value for the formaldehyde hydration reaction. Particularly, the combination of M06-2X with 6-311+G(d,p) provides the lowest absolute deviation value for the enthalpy change of the formaldehyde hydration reaction ($-0.07 \text{ kcal mol}^{-1}$).

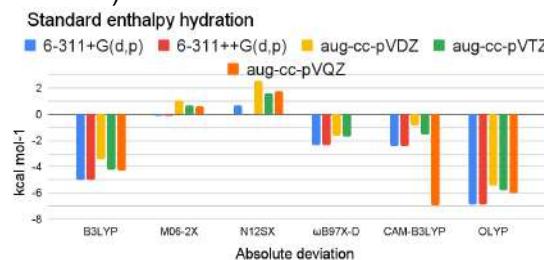


Fig.2. Absolute deviation obtained with each functional for standard enthalpy hydration

Afterwards, the obtained values, with the different functionals, will also be compared with the values obtained by the reference method CCSD(T), using the aug-cc-pVQZ basis set. In future steps, the validation of the method will be done through the evaluation of the formaldehyde trimerization reaction and the reaction paths for the capture of H₂S will be simulated with different aldehydes used industrially.

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Remodelagem da Superfície de Energia Potencial da reação



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Palavras-Chave: Superfície de Energia Potencial; Pontos estacionários.

Introdução

A superfície de energia potencial (SEP) é uma função que mostra a relação matemática entre a energia potencial sentida pelos átomos e as configurações geométricas, descrevendo as interações às quais os núcleos atômicos estão sujeitos. As SEPs podem ser representadas pela seguinte fórmula:

$$V: \Omega \subset R^n \rightarrow R,$$

onde o Ω é um conjunto que representa as possíveis configurações nucleares (com alguma parametrização apropriada) e V é definida por:¹

$$V(x) = E_{elec}(x) + E_{nuc}(x),$$

onde E_{elec} e E_{nuc} correspondem a energia eletrônica e nuclear, respectivamente, em uma configuração nuclear $x = (x_1, x_2, \dots, x_n)$. Obter uma representação acurada da SEP permite determinar mais corretamente os pontos estacionários, bem como as propriedades da reação química. Esses pontos caracterizam mínimos (espécies estáveis) ou pontos de sela (estados de transição).²

O cálculo de SEPs com métodos de alto nível pode ser computacionalmente inviável, pois muitos pontos tem de ser calculados. Por outro lado, as energias relativas dos pontos estacionários muitas vezes pode ser obtida com métodos muito mais precisos. É, portanto, de grande interesse poder modificar uma SEP (calculada com um método não tão acurado) para que seus pontos estacionários possuam as energias calculadas por métodos mais rigorosos, mas sem destruir a topologia global da SEP.

O trabalho tem como objetivo modificar a SEP³ da reação $F + H_2O \rightarrow HF + OH$ para que os pontos estacionários reproduzam as energias relativas obtidas através dos cálculos de estrutura eletrônica mais acurados, como o método coupled-cluster multirreferencial (MRCC).

Metodologia

Foi utilizado o código que calcula a SEP da reação $F + H_2O \rightarrow HF + OH$.³ Apesar de originalmente em fortran, nossos cálculos são realizados através de uma interface que criamos em Python.

Os pontos estacionários da SEP cujas energias relativas procurou-se alterar foram: os produtos ($OH + HF$), o estado de transição e dois mínimos de van der Waals (um na região dos reagentes e outro na região dos produtos). Para

otimizar as geometrias destes pontos estacionários usamos tanto a biblioteca scipy (função minimize) quanto um algoritmo de Newton que implementamos.

Para modificar as energias relativas usamos a seguinte expressão:

$$V(x) = V_{orig}(x)c(x),$$

onde $c(x)$ é uma somatória de gaussianas:

$$c(x) = 1 + \sum_k (c_k - 1)e^{-\sum_i a_i^k (x_i - r_i^k)^2},$$

cujos parâmetros c_k e a_i^k são escolhidos para se obter uma modificação o mais suave possível que forneça as energias relativas que procuramos. Isso é feito através na análise de gráficos dessa função, de modo a obter uma variação suave em torno de 1.

Resultados

Foi possível observar que as energias relativas do estado de transição pôde ser ajustada para coincidir com o valor procurado. As energias relativas dos mínimos de van der Waals são mais difíceis de serem reproduzidas, provavelmente por serem poços muitos rasos.

As geometrias dos pontos estacionários sofreram poucas modificações com relação às geometrias originais.

Conclusões

Concluímos que é possível realizar modificações na SEP utilizando uma modificação simples, mas é necessário realizar uma análise cuidadosa dos gráficos da superfície. Esses princípios podem ser aplicados em outras SEPs. Futuramente faremos modificações para ajustar também as geometrias de equilíbrio e frequências vibracionais.

Agradecimentos

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Estudo computacional das interações de moléculas de surfactante com nanoestruturas de ouro.

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Palavras-Chave: Termodinâmica de superfícies; Interação ouro-surfactante; Dinâmica Molecular

Introdução

Surfactantes são moléculas essenciais para processos de síntese, estabilização e modificação pós-sintética de nanoestruturas de diversos metais, como os de ouro. No entanto, seus mecanismos em escala molecular não são ainda plenamente conhecidos. Faz-se então necessário realizar simulações de dinâmica molecular (MD) de diferentes estruturas coloidais de surfactantes interagindo com as principais faces cristalinas do ouro. Porém, os campos de força disponíveis para descrever as interações do ouro com moléculas adsorvidas não foram parametrizados a fim de reproduzir sua energia livre de adsorção, utilizando apenas um potencial clássico simplista de Lennard-Jones. Além disso, as nanoestruturas de ouro utilizadas nessas simulações, não sofreram um estudo detalhado e sistemático para diferentes geometrias a respeito de sua estabilidade, tanto para sistemas bulk, quanto para sistemas interfaciais. Dessa forma, o trabalho apresentado pretende estudar simulações de dinâmica molecular envolvendo diferentes nanoestruturas de ouro e fazer a validação de um potencial clássico polarizável¹ para descrever a interações ouro com H₂O, Br⁻ e CTA⁺.

Metodologia

As simulações de dinâmica molecular para verificar a estabilidade de nanoestruturas de ouro foram feitas com o programa GROMACS 2019.6. As simulações foram feitas no ensemble NPT e os sistemas investigados incluem as nanoestruturas de ouro com direções cristalográficas {100} e {111}. Realizou-se um otimização de geometria das moléculas alvo com o ouro, a fim de achar uma distância otimizada que foi utilizada para os cálculos single point, que por sua vez, foram feitos com o potencial clássico polarizável, e com potencial quântico, GFN1-xTB. As energias calculadas são então comparadas individualmente a fim de validar o potencial.

As estruturas Au-moléculas alvo buscam ser as mais representativas possíveis, tal que com poucas rotações das moléculas e poucos pontos de grid ao

redor do ouro, consegue-se varrer os principais planos cristalinos. As distâncias escolhidas foram retiradas da otimização, escolhendo também distâncias mais curtas e longas, validando assim a parte repulsiva e dispersiva do potencial.

Resultados

As simulações de MD mostraram que todas as estruturas de ouro são estáveis, havendo flutuações nas componentes de energia, mas estabilização em um patamar. Além disso, para todos os sistemas investigados não houve deformações ou irregularidades significativas nas estruturas, notando-se apenas oscilações normais. A otimização de geometria trouxe como distâncias de equilíbrio 2,54 e 2,60 Å, para o brometo e água, respectivamente.

A parte de validação do potencial encontra-se ainda em etapas preliminares, em que estão sendo calculados single-points quânticos e clássicos de 12 estruturas Au-Br⁻ em torno de 30 para Au-H₂O e Au-CTA⁺. Além disso, serão feitas simulações de MD de monocamada de CTAB adsorvidas nas superfícies cujos potenciais foram validados.

Conclusão

O trabalho apresentado mostra a estabilidade do ouro em diferentes nanoestruturas, através de simulações de MD. Além disso, distâncias otimizadas foram encontradas para H₂O-Au e Br⁻-Au. Os resultados para a validação e para MD de monocamada de CTAB, embora não finalizados ainda, revelam-se animadores.

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Enrijecimento da estrutura de silício com nitrogênio: uma aplicação em baterias.

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Palavras-Chave: Silício, Baterias, Impurezas, DFT.

INTRODUÇÃO

Para suprir as atuais demandas energéticas dos dispositivos eletrônicos, assim como meio para o armazenamento de energia provenientes de fontes eólicas, solar e biológicas, as baterias de íons de lítio (LIB - Lithium-ion Battery) tem sido as mais utilizadas. A sua ampla utilização é justificada devido ao seu longo ciclo de vida, alta densidade de energia, segurança e leveza¹. As LIBs recarregáveis disponíveis comercialmente possuem o material do ânodo feitos de grafite, no qual é litiado para LiC_6 com capacidade teórica de 372 mAh g^{-1} . Sendo assim surge a necessidade de encontrar novos materiais anódicos com capacidade teórica maiores e que atendam os critérios básicos que viabilizem sua comercialização. Devido a sua abundância, baixo preço, baixa toxicidade, e principalmente sua alta capacidade específica de 4200 mA h g^{-1} com baixo potencial de trabalho, o silício (Si) apresenta-se como um material promissor para substituir o grafite como material do ânodo². No entanto, existem dois fatores críticos que impedem o uso comercial do Si como material anódico. O primeiro é o aumento significativo na mudança do volume durante os processos de carga e descarga, com um aumento de > 300% que leva a desintegração do eletrodo, perda de contato com os coletores de corrente, reações colaterais com os eletrólitos, e rápido decaimento da capacidade e tempo de vida. O segundo está relacionado com sua baixa condutividade elétrica e baixos coeficientes de difusão Li^+ . Dessa forma, é necessário realizar pesquisas que possam ajudar a solucionar esses problemas dos ânodos a base de silício. Um método comum para melhorar as propriedades eletrônicas e estruturais dos materiais, consiste na dopagem com diferentes elementos químicos.

METODOLOGIA

Como ponto de partida estrutural, utilizamos uma célula unitária cúbica de face centrada na conformação de diamante contendo oito átomos de Si. Posteriormente verificaram-se os sítios de simetria e então os átomos de silício foram substituídos por átomos de lítio e nitrogênio. Os cálculos foram realizados utilizando a Teoria do Funcional da Densidade, dentro da aproximação GGA juntamente com o funcional de troca e correlação PBE. Utilizaram-se pseudopotenciais ultra macios de norma-conservada Troullier-Martins, USPP. Todos os cálculos foram realizados fazendo-se o uso do pacote Quantum Espresso³. Após a

otimização das geometrias, avaliamos as estruturas eletrônicas, a densidades de estados e o bulk modulus a fim de obter uma relação entre a resistência da estrutura e o tipo de impureza.

RESULTADOS

Resultados preliminares mostraram que a presença do nitrogênio favorece a estabilidade da estrutura, assim como o composto formado torna-se condutor. Com o aumento da quantidade de impurezas a estrutura se torna mais rígida, dessa forma acreditamos que o composto formado seja mais resistente a fraturas, permitindo assim a viabilidade da utilização do silício com material anódico.

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Second Virial Coefficient for the H₂ ... Cl₂ gaseous mixture

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Palavras-Chave: second virial coefficient, H₂ ... Cl₂, potential energy surface.

INTRODUCTION

In the past few years we have been working in developing potential energy surface (PES) using the spherical harmonic expansion. To this end, we freeze the interatomic distance of each monomer at the equilibrium distance optimized for each basis set as a rigid rotor. This approach allows us to perform all necessary calculations with lower computational cost. In principal, the rigid rotor generates relatively good values for the second virial gaseous property in the interval of temperatures of interest. As a prototypical function for the analytical potential we use the Pirani *et al.* potential function:

$$V(R, \gamma) = \varepsilon \left[\frac{m}{n(R, \gamma) - m} \left(\frac{R}{R_m} \right)^{n(R, \gamma)} - \frac{n(R, \gamma)}{n(R, \gamma) - m} \left(\frac{R}{R_m} \right)^m \right]$$

where R is the distance between the centers of the monomers and $\gamma \equiv (\theta_1, \theta_2, \phi)$, according to the well known Jacobi coordinates. m, R_m, ε are a free parameter, minimum position of the well, and the depth of the well respectively. $n(R, \gamma)$ is given by

$$n(R, \gamma) = \beta + \alpha \left(\frac{R}{R_m} \right)^2$$

where β e α are free parameters here. It has been proved that this prototypical function captures correctly the R^{-6} behavior of the potential. The anisotropy of the analytical PES is obtained through the spherical harmonics expansion using eight leading configurations (LC) with the three fixed angles (θ_1, θ_2, ϕ): H($\pi/2, \pi/2, 0$), L($0, 0, 0$), T_a($0, \pi/2, 0$), T_b($\pi/2, 0, 0$), S_a($\pi/4, \pi/3, \pi/2$), S_b($\pi/3, \pi/4, \pi/2$), Z($\pi/4, \pi/4, 0$), and X($\pi/2, \pi/2, \pi/2$). The spherical harmonics expansion includes the v⁰⁴⁴ and the v⁴⁰⁴ moments, the second one is repulsive like the v²²⁰ moment. v⁰⁰⁰ is the isotropic term and can be measured experimentally. To our knowledge, there is no data for the second virial coefficient for H₂-Cl₂ system.

METHODOLOGY

In a previous paper for the H₂...F₂ system, we sketched the recipe to obtain the analytical PES for similar systems with A₂...X₂ to take account the anisotropy. We use Molpro to calculate a set of 100 *ab initio* points at varying intermolecular distances

2.0 ≤ R ≤ 12.0 Å, for each LC, at the CCSD(T)/aug-cc-pVXZ level, with X = D and T, and use the CBS extrapolation for the energies: $E_k = E_\infty - a/k^3$, with k = 2, 3 for DZ and TZ respectively. As a good test we perform calculations to obtain the second virial coefficient for such a system. The classical and the respective quantum corrections are given in the expansion

$$B_2(T) = [B_{cl}(T) + B_r^r(T) + B_I^{a,I}(T) + B_I^{a,\mu}(T) + \dots]$$

B_{cl} is the classical second virial coefficient. It is usually referenced as a lower bound for this physical parameter. It is given by:

$$B_{cl}(T) = -2\pi N_A \int (e^{-U(\Omega)/RT} - 1) \Omega^2 d\Omega$$

where $U(\Omega)$ is the PES and $\Omega = (R, \theta_1, \theta_2, \phi)$, N_A is the Avogadro number. The other coefficients of the expansion are the radial and angular quantum corrections whose expressions can be found in [J. Chem. Phys. **78**, 7217 (1983)] or in our previous work [Chem. Phys. Let. **779**, 138845 (2021)].

RESULT

The most stable LC is the T_b, with energy of 24.1 meV and distance of 4.003 Å while the less stable is the L one with energy of 4.7 meV and distance of 4.487 Å. For the system analyzed here the isotropic distance are 3.999 Å with 11.838 meV energy and the difference among the minimum and the extended model are less than 0.1meV. The equilibrium distances for each monomer were obtained at the same basis set level getting 0.744 Å for the H₂ and 2.008 Å for the Cl₂ molecules. These results are in good agreement with the experimental data, i.e., 0.741 Å for H₂ and 1.988 Å for Cl₂ molecules.

Long Meng and Estela-Uribe and Jaramillo developed some empirical correlation equation for the second virial coefficient, based on the so-called pseudocritical parameters, such as critical pressure, temperature and densities, which we used here to compare our results.

ACKNOWLEDGMENT

FAPESP

Complex eIF4E- eIF4G Inhibitors for the Treatment of Autistic Spectrum Disorder: A theoretical study

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Keywords: Conformational information, chemical interactions, pharmacodynamics

Introduction

Autism spectrum disorder (ASD) encompasses a distinct group of disorders related to neurodevelopment. This fact makes it difficult to accurately find strategies that enable the diagnosis and treatment of this type of disorder. However, recent scientific discoveries point to protein synthesis as an interesting path to be explored. In this sense, this work aims to investigate the complex eIF4E-eIF4G, which is already used in cancer treatment, as a potential drug in the treatment of ASD through computational tools¹. For this purpose, with this purpose, the pharmacophoric site of the 4EGI-1, an inhibitor of this complex, was used as the basis for the computational technique of virtual screening. The principle is based on the search for the ligand according to the similarity of known active molecules. After the screening phase, the filtered compounds went through molecular docking, a computational tool belonging to molecular mechanics capable of measuring the degree of interaction between a ligand and the target molecule. The docking method has the ability to generate 3D poses, which makes it possible to predict the most likely bioactive conformation of ligands within the binding site of the macromolecule. Lastly, we aim to find ligands at least as promising as 4EGI-1, and evaluate their effects in the treatment of autistic individuals.

Materials and Methods

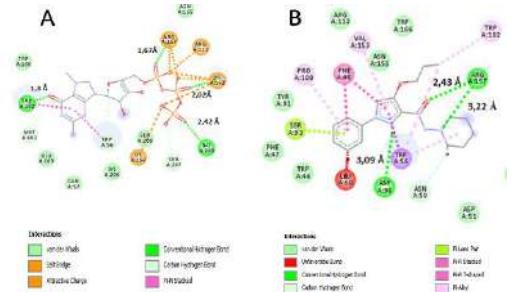
Initially, the pharmacophoric part of the 4EGI-1 ligand was reconstructed in three dimensions. This model was the basis for virtual screening on databases such as PHARTMIT and the ZINC PHARMER, which resulted in more than 600 binders². To select molecules with promising pharmacokinetic profiles, Lipinski's rule of five was applied. The potentially toxic ligands were eliminated after going through a filtering step in FAF-drugs4, leaving 167 promising molecules. Before performing molecular docking, the promising structures were computationally optimized in the Gaussian 09W program using DFT B3LYP 6-31G* level of theory³. Charge calculation of the structures was performed in m PC Spartan® (version Pro, Wavefunction, Inc., Irvine, CA, USA). The crystallized structure of the protein eIF4E was retrieved from the Protein Data Bank (PDB:4PTW) and was also prepared before docking. Charge calculations and hydrogen addition were performed in the Discovery Studio® 3.5. Finally, molecular docking

calculations were carried out in the MVD® (Molegro Virtual Docker) program⁴.

Results and Discussion

After docking the 167 ligands, we noticed an interesting outcome, one of the ligands presented an interaction energy lower than that obtained in redocking (-131.63). The ligand we will call 1 has the lowest energy of ligand-protein interaction (-154.00), which makes it the most stable at the active site, once the affinity ligand-receptor is measured by the preferred orientation and minimum binding energy. Figure 1 is a comparison between the interactions made by the crystallized ligand from redocking (A) and the ligand 1 (B). We can observe that even with a smaller number of hydrogen bonds below 2.5 Å, the interaction energy of B remains a greater factor, which indicates that other types of interactions, such as van der Waal, hydrophobic and electrostatics, contribute to the stabilization of the ligand³. It is also possible to observe that amino acid residues Arg 112, Arg 157, Trp 56, Met 101 are present in both structures, an indication of their importance for linker stabilization.

Figure 1. Types of interactions of ligand A and B with eIF4E protein residues.





First principles investigation of Si-doped BC₂N single layer for Hydrogen storage and Hydrogen Evolution Reaction (HER)

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Palavras-Chave: BC₂N, Density Functional Theory, Si-doped.

In recent years, both experimental and theoretical studies have demonstrated that BN nanomaterials exhibit high H₂ uptake capacity due to the stronger interactions of the heteropolar B e N bonds and the H₂ molecules¹. The ternary BCN nanomaterials present intermediate properties between carbon and BN and the electronic properties can be tuned varying stoichiometry. These ternary nanomaterials have been synthesized and exhibit a high surface area and with remarkable adsorptive properties. The BC₂N stoichiometry is believed to be one of the most stable. Liu et al. have predicted that the BC₂N present three possible atomic arrangements which are named as model-I, model-II and model-III, which differs on the type and number of bonds between the three atomic chemical species involved². Their results indicate that the model-I are metallic while the model-II and model-III exhibit semiconducting properties. Our previous theoretical calculations show that the type-II nanostructures are semiconductor with a band gap of about 1.6 eV and are more stable by 1.0 eV per BC₂N unit (four atoms) compared to type-I and type-III, a result that may be attributed to the large number of stable C-C and B-N bonds³. To increase adsorption capacity and surface reactivity, atomic doping is a powerful feature. In this study, using density functional theory (DFT) calculations we investigate the structural, energetic and electronic properties of Si-doped BC₂N single layer arranged in the hexagonal network. The Si atom substitute a X atom (X = C, B or N) to functionalize the BC₂N single layer. We investigate the possibility to use the functionalized BC₂N single layer for H₂ storage by calculated the free energy diagrams and the hydrogen evolution reaction (HER) process. DFT calculations are performed with the Vienna *ab initio* simulation package (VASP) within generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (PBE) to modulate the exchange-correlation functional. The basis set is constructed using plane waves with a kinetic energy cutoff of 500 eV. To calculate the periodic functions, the k-points in the Brillouin zone (BZ) are generated using the Monkhorst-Pack (MP) scheme with a 5x5x1 grid. To obtain the energetic stability of the pristine and functionalized structures the conjugated gradient (CG) method is used and the forces on the

atoms are calculated using the Hellmann-Feynman procedure. In our calculation no constraints are imposed, all atoms in the supercell are allowed to relax (until the forces are smaller than 0.01 eV/Å) without imposing any symmetry. The dispersive forces are modeled through the DFT-D2 method of Grimme to obtain the adsorption energies between the Si-doped system and the H₂ molecules. We observed that the most stable site (lower formation energy) for the Si atom is in replace of C atom (type II) that bonds with two C and one N atoms (Si_{Cl}). For all the cases, the Si atom moves out of the plane forming a buckling in the monolayer. The semiconductors properties are maintained with two spin electronic levels inside the band gap when Si atom replaces a B and a N atom. The adsorption energies when the H₂ molecules are introduced range between 50 and 80 meV which are greater as compared to the pristine (non doped) system. These results also indicate that the doped BC₂N layer can be used for the HER process in the water splitting. In addition, we observe that the dispersive forces (van der Waals interactions) are responsible by circa 50% of the adsorption energies.

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Comparative analysis among different structural minimization methods based on Branch-and-Prune structural reconstruction algorithm

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Keywords: SARS-CoV-2, P.1 variant, computational optimization

1. Introduction

As the SARS-CoV-2 virus spreads through the human population, more variants of concern emerge [1]. However, there is a long delay between recognizing a new variant and obtaining its crystallographic structure. Thus, in this research we show the results obtained with a Branch-and-Prune (BP) implicit enumeration algorithm, that reconstructs the best conformation from the theoretical NMR data for ACE2-RBD complex, now added with P.1 variant. In this way, the algorithm enumerates all the possible positions based on interatomic distances while discarding the invalid ones. Finally, the resulting structure was validated by the Ramachandran diagram and refined by structural minimization.

2. Methodology

Initially, we implemented mutations K417T, E484K and N501Y that constitute the P.1 variant with PyMOL 2.3 for the ACE2-RBD complex. Then, instances of tests for the problem were generated by simulating the NMR data (an arbitrary set of distances with distances less than 6Å). After that, the structure was reconstructed using the BP algorithm and compared with the crystallography obtained recently (PDB ID: 7NXC) [1].

The BP algorithm used is an implicit enumeration method which builds a binary tree in which each level represents possible spatial positions for an vertex, each atom of the protein generates two possibilities for positions valid in the plane. Pruning is done using the Direct Distance Feasibility (dff) method which considers known distances to the vertice that have not been used to determine your position, if it is not a valid embedding so any subtree below is pruned [2]. The percentage of amino acids in the most favorable region of the Ramachandran diagram was calculated by the MolProbity server [3]. The potential energy was calculated by the Prime algorithm implemented in the Schrodinger Maestro 2021-2 software [4], which was also used in all minimization methods and structure visualization.

3. Results and Discussion

The structural reconstruction of the P.1 variant was very consistent as the RMSD in alignment with crystallography was only 0.483Å (see Figure 1). After the structural reconstruction using BP algorithm, we performed a minimization using a conjugate gradient. The potential energy (see Table 1) was -33060.39 kcal/mol while 97.4% of the amino acids

were in the most favorable region of the Ramachandran diagram.

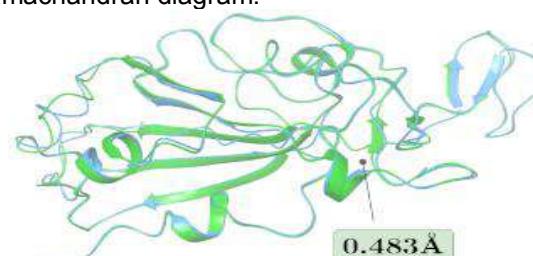


Figure 1: Alignment between the output structure of BP algorithm and the crystallography with P.1.

Therefore, by minimizing the structure, it became even more consistent than that obtained recently in the Protein Data Bank (PDB ID: 7NXC) with 95.0%.

Table 1: Comparison among different structural minimization methods for the ACE2-RBD complex. In all softwares, the best solution of the BP algorithm was used as input for minimization.

Minimization Methods	Potential energy (kcal/mol)	Favourable residues (%)
Without minimization	-25768.23	97.1%
Conjugate gradient (Prime)	-33060.39	97.4%
Simulated annealing (Desmond)	-23739.09	72.7%
LBFGS (Desmond)	-32523.4	94.1%
Simulated annealing (NAMD)	-20998.0	92.9%

4. Concluding Remarks

BP algorithm presented a consistent reconstruction for P.1, since without minimization the number of residues in the favorable region was 97.1% while RMSD in alignment with the crystallographic structure was 0.483Å. Finally, the conjugate gradient method proved to be the most promising method to improve the quality of structural prediction.

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Theoretical characterization of the properties of zinc and silicon phthalocyanines with possible application to solar cells.

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Keywords: Phthalocyanines, DFT, Solar cells

There is currently a great demand for energy worldwide, driven by the growth of the world's population. However, current energy sources are highly polluting, so it is necessary to search for new energy sources. One of them is dye-sensitized solar cells, where phthalocyanines play an important role. Phthalocyanines with divalent metals such as Zinc have been widely used, however, phthalocyanines (Pcs) with tetravalent metals have been less studied. Therefore, Zn and Si Pcs with periplanar and axial substituents, respectively, (**Figure 1**) have been designed.

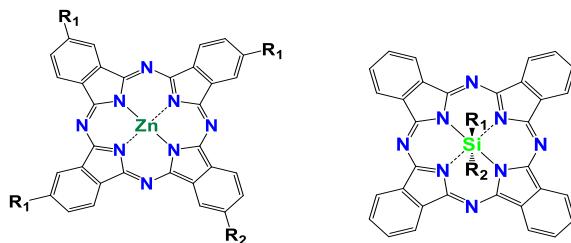


Figure 1. Molecular structure of the Zn- and Si-phthalocyanines studied

Several donor groups (hydroxyl, primary amines, secondary amines, amide, and ester) and different anchoring groups (carboxyl, anhydrous and catechol), which are shown in **Table 1** were evaluated. These modifications are produced to be evaluated for possible application in dye-sensitized solar cells. The effect of these modifications on the optical and electronic properties in each of the 66 molecules has been investigated from a theoretical point of view. Optimized molecular structures at the B3LYP/6-31G(d,p) level of theory with Grimme's dispersion show non-planar systems suggesting a lower tendency to aggregation of phthalocyanines. It was also found that all structures have a LUMO energy level higher than the energy of the conduction band edge of the semiconductor (TiO_2) suggesting a better injection of electrons between dye and semiconductor. Considering the electron injection, ZnPc exhibit higher values compared to SiPc, with primary amine and secondary amine substituents. According with the NBO analysis it was found an intramolecular charge transfer from carbons to indole nitrogen and azo bridges, in addition it was evidenced that the indole nitrogen has less charge to be directly bond to the metal. Electrostatic potential maps show a concentration of electrons in the substituents

groups, thus showing the donor effect that they have on the system. In addition, the optical properties showed the characteristic bands, an intense band Q close to 700 nm and the B band around 350 nm, being the compound 9 with silicon and the anhydro anchoring group the one that greater wavelength present.

Substituents groups (R_1)		
<chem>CC1=CC(Oc2ccccc2)C(Oc3ccccc3)=C1</chem> 1	<chem>CC1=CC(Oc2ccccc2)C(Oc3ccccc3)=C1</chem> 2	<chem>CC1=CC(Oc2ccccc2)C(Oc3ccccc3)=C1</chem> 3
<chem>CC1=CC(Nc2ccccc2)C(Oc3ccccc3)=C1</chem> 4	<chem>CC1=CC(Nc2ccccc2)C(Oc3ccccc3)=C1</chem> 5	<chem>CC1=CC(Nc2ccccc2)C(Oc3ccccc3)=C1</chem> 6
<chem>CC1=CC(Nc2ccccc2)Nc3ccccc3</chem> 7	<chem>CC1=CC(Nc2ccccc2)Nc3ccccc3</chem> 8	<chem>CC1=CC(Nc2ccccc2)Nc3ccccc3</chem> 9
<chem>CC1=CC(Oc2ccccc2)Nc3ccccc3</chem> 10	<chem>CC1=CC(Oc2ccccc2)Nc3ccccc3</chem> 11	

Anchoring groups (R_2)		
<chem>CC1=CC(Oc2ccccc2)C(=O)O</chem> Carboxyl	<chem>CC1=CC(Oc2ccccc2)C(=O)OC(=O)C</chem> Anhydrous	<chem>CC1=CC(Oc2ccccc2)C(Oc3ccccc3)=C1</chem> Catechol

Table 1. Molecular structure of the substituents studied.

Acknowledgments. We are grateful for the financial support of ANID/CHILE under FONDECYT Project 1171719 (G.C.-J.). Powered@NLHPC: This research was partially supported by the supercomputing infrastructure of the NLHPC (ECM-02) of the Universidad de Chile. This work was funded by the National Agency for Research and Development (ANID) / Scholarship Program / DOCTORADO BECAS NACIONALES/2021 – 21210406.

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Estudo QSAR de análogos aos rubrolídeos e suas lactamas derivadas com atividade contra *S. aureus*.

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Palavras-Chave: Rubrolídeos, *S. Aureus*, QSAR.

INTRODUÇÃO

Com o aumento de bactérias multirresistentes, o desenvolvimento de novos fármacos com atividade antimicrobiana têm grande importância. Em um estudo recente realizado [1], novos compostos análogos aos rubrolídeos e seus derivados lactâmicos foram sintetizados e suas atividades antimicrobianas foram avaliadas contra *S. aureus*.

O planejamento de fármacos através da análise das Relações Quantitativas Estrutura Atividade QSAR (do inglês Quantitative Structure-Activity Relationship) permite prever a atividade de moléculas antes de sintetizá-las, facilitando o processo.

No presente trabalho, é apresentado um estudo de QSAR-3D e 4D LQTA-QSAR [2], em que foi utilizado um conjunto de 29 compostos com atividade biológica contra *S. aureus* relatado no trabalho de Miranda et al. [1].

METODOLOGIA

Os compostos foram desenhados no programa Chemsketch e suas geometrias foram otimizadas pelo método semi-empírico AM1 e na sequência por DFT B3LYP/6-311G(d,p) utilizando o programa Gaussian. Com as moléculas otimizadas, foram gerados perfis de amostragem conformacional (PAC) de cada molécula por simulação de dinâmica molecular, utilizando a biblioteca Python OpenMM.

Uma estrutura comum a todos compostos foi selecionada (Figura 1) e todas moléculas e os PAC foram alinhadas com base nessa estrutura. As moléculas que passaram apenas por alinhamento foram utilizadas para gerar descritores 3D, e os PAC alinhados para gerar os descritores 4D aplicando a metodologia LQTA-QSAR [2].

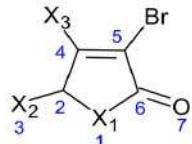


Figura 1. Estrutura usada para alinhar os compostos. As numerações se referem a ordem utilizada no alinhamento.

Os descritores 3D e 4D foram gerados pelo programa LQTAGrid, que considera as moléculas dispostas em um grid tridimensional, onde são calculadas as energias de interação com uma sonda (NH_3^+) em cada ponto desse grid.

Após gerados os descritores, os conjuntos de dados foram submetidos ao programa QSARMode-

ling [3], onde foi aplicado algoritmo genético para selecionar os descritores. Com as matrizes de descritores selecionados, foi feita uma nova seleção de variáveis, utilizando uma busca sistemática.

Os modelos obtidos foram validados internamente por validação cruzada, aplicando a estratégia leave-one-out. Sobreajuste e correlação ao acaso foram avaliados aplicando o método de aleatorização de y . A robustez do modelo foi avaliada por validação cruzada com leave- N -out (N de 1 a 7).

Após a validação interna, os dois modelos foram validados externamente utilizando um mesmo conjunto teste, determinado aleatoriamente, mas cobrindo uma boa faixa de valores de atividade.

RESULTADOS E CONCLUSÕES

O melhor modelo 3D foi construído com quatro descritores e duas variáveis latentes, enquanto o modelo 4D foi construído com seis descritores e duas variáveis latentes. Ambos modelos mostraram-se robustos e precisos, conforme as estatísticas da validação interna e externa mostradas na tabela 1. Em ambos modelos observou-se que para uma das moléculas mais ativas ((Z)-3-bromo-4-(5-bromo-2-metoxifenil)-5-(2,5-dimetoxifenil)-5-hidroxi-1-isobutil-1H-pirrol-2(5H)-ona) há uma proximidade dos descritores 3D e 4D com átomos de oxigênio, indicando que estes podem ser importantes para a atividade.

Tabela 1: Dados estatísticos da validação interna (CV) e externa (VE) obtidos para o modelo.

Parâmetros	Modelo 3D	Modelo 4D
R^2_{CV}	0,8873	0,8594
Q^2_{CV}	0,8387	0,8171
R^2_{VE}	0,8747	0,8388

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THEORETICAL STUDY OF BIO-DIESEL VISCOSITY AND DENSITY USING MOLECULAR DYNAMICS

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Keywords: molecular modeling, liquid property, ethyl ester.

INTRODUCTION

Biodiesel is a biofuel formed by a mixture of methyl or ethyl fatty acid esters, obtained from the transesterification reaction involving a triglyceride compound and an alcohol¹. According to the literature, we obtained the physical properties for some fatty acid ethyl esters (FAEE) biodiesel compounds. Our study has proposed a simple and efficient methodology to comprehension and theoretical calculation of density and viscosity of ethyl ester bio-diesels.

MATERIALS AND METHODS

We chose to simulate the ethyl ester bio-diesels from three different oil sources: canola (CNE), sunflower (SFE), and linseed (LSE). Table 1 shows the parameters for ethyl ester bio-diesels, including the weight fraction (wt%) composition for each bio-diesels² and the number of molecules for Molecular Dynamics (MD).

Table 1: Fatty acid ethyl ester (FAEE) composition (wt%) of biodiesel esters and the number of FAEE molecules in MD biodiesel boxes.

Biodiesel Ethyl ester	Total # molecules	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)	Ref. for composition
Canola	993	4.4 (47)	2.3 (22)	69.4 (683)	18.0 (181)	5.9 (60)	2
Sunflower	991	6.3 (66)	4.7 (45)	21.0 (204)	68.0 (675)	0.0 (0)	2
Linseed	1004	5.1 (54)	3.1 (30)	13.7 (133)	15.2 (151)	62.9 (636)	1,3

Initial structures for each FAEE were obtained by geometry optimization. A biodiesel FAEEs boxes were obtained using Packmol⁴. The equilibration stage was performed in two different ways: a) 2 ns NpT MD at 313.15 K and 1 bar; b) 1 ns NpT MD at 298.15 K and 1 bar followed by 1 ns NpT MD at 313.15 K and 1 bar. All production simulations were performed using the pmemd.cuda module of AMBER18.

RESULTS AND DISCUSSIONS

According to the Stokes-Einstein formula, the diffusion coefficient D of a spherical body of radius a in a fluid with viscosity is given by

$$D_i = \frac{k_B T}{6\pi\eta_i a_i} \quad (1)$$

and using the relation for viscosity calculation with different compounds:

$$\ln \eta_m = \sum_{i=1}^n y_i \ln \eta_i \quad (2)$$

We can rewrite the Eq.(2) by:

$$\ln \eta_m = \ln \frac{k_B T}{6\pi} - \sum_{i=1}^n y_i \ln D_i a_i \quad (3)$$

Using MD simulations of biodiesel systems, we can obtain its density and the parameters for each FAEE: D_i , a_i (we chose to use the average radius of gyration for each FAEE), and y_i (the wt%, according to Table 1). Therefore, we can determine the viscosity for the bio-diesel fuel.

CONCLUSION

We have proposed a new methodology to calculate by MD simulations some physical properties of bio-diesel fuels. Our methodology was simple and effective for density and viscosity determination. The values obtained came close to those found in the literature. New applications of our methodology can be performed for other biofuels from different oil sources.

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DFT Study on the influence of β -cyclodextrins as support in the interaction between a Pd_4 cluster and chlorobenzene

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Keywords: Cyclodextrin, DFT, C-C bonding coupling reactions.

INTRODUCTION: Currently, most of the organic molecules used in drugs and pharmaceutical intermediates and precursors, are synthesized via Pd-catalyzed C–C coupling reactions, including Heck, Suzuki and Negishi reactions.¹ Recent studies have been shown that the employ of Pd nanoparticles on β -cyclodextrin (β CDs) leads an increase of the efficient these reactions, providing an environment friendly medium and with high catalytic activity.^{2,3} However, the full comprehension about the possible mechanisms responsible by behavior this catalytic system is still a big challenge. Thus, the present study has been investigated computationally the possible alterations promoted by a β -cyclodextrin monomer in the interactions between a Pd cluster and aryl halides, an important step in Heck, Suzuki and Negishi reactions.

METHODOLOGY: Firstly, the β CD monomer was constructed with aid of the experimental parameters obtained in literature.⁴ One tetrahedral Pd_4 cluster was approximated of the hydrophobic (HYPB) and hydrophilic (HYPL) regions of the β CD monomer. Each configuration produced was used as starting point for structural optimization calculation. Thereafter, a single molecule of chlorobenzene (C_6H_5Cl) was submitted to interaction with the Pd_4/β CD arrangements of lowest energy. All calculations were performed at B3LYP/LANL2DZ/6-31G(d,p) DFT level. However, the Cl atom was described with the 6-311G(d) basis set. The interaction energies were corrected with the counterpoise method to eliminate the BSSE. The charge transfers and intensity of the interactions within the optimized complexes were evaluated through NBO method. All complexes present the singlet state as the lowest energy state.

RESULTS: The results of interaction energy show that Pd_4 cluster interacts more strongly with the HYPB center than the HYPL moiety of β CD ($-32.0\text{ kcal mol}^{-1}$ against $-22.1\text{ kcal mol}^{-1}$). The chlorobenzene molecule adsorbs on Pd_4 in HYPL moiety with energy 4.7 kcal mol^{-1} greater than in HYPB center ($-17.8\text{ kcal mol}^{-1}$ against $-13.1\text{ kcal mol}^{-1}$). When the β CD coordinates are withdraw of the complexes, the C_6H_5Cl/Pd_4 interaction energy increases 3.1 kcal mol^{-1} for HYPB complex, whereas in HYPL, it decreases in 0.5 kcal mol^{-1} . The interaction of β CD by means of its HYPL part with Pd_4

leads to the di- σ adsorption mode for C_6H_5Cl (Fig 2.a"). When Pd_4 is placed in the HYPB cavity, the C_6H_5Cl prefers to adsorb in π mode (Fig. 2b").

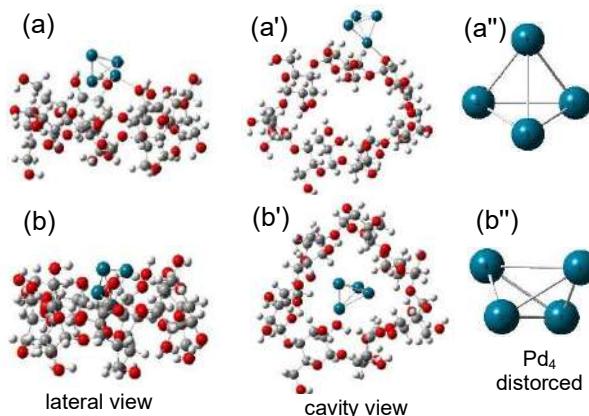


Fig.1. Conformations of lowest energy for Pd_4 complexed in β CD, in HYPL (a and a') and HYPB (b and b'), and isolated (c and c').

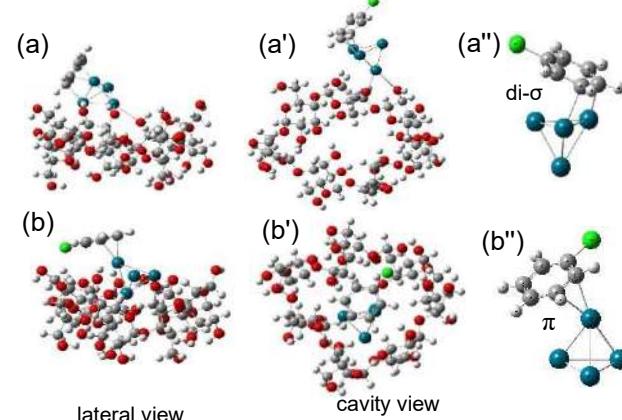


Fig 2. Conformations of lowest energy for β -CD/ Pd_4/C_6H_5Cl in HYPL (a, a' and a'') and HYPB (b, b' and b'').

CONCLUSIONS:

The β CD influences more strongly in the $Pd_4-C_6H_5Cl$ interaction through its hydrophobic cavity. However, this interaction is more energetic when Pd_4 is deposited on the hydrophilic part of β CD.

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Estudo computacional do mecanismo da reação de Suzuki-Miyaura catalisada por níquel, envolvendo sal de arenodiazônio em glicerol

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Palavras-Chave: Suzuki-Miyaura, níquel, glicerol

Introdução

Com o crescente interesse em sistemas ambientalmente mais amigáveis, muitos protocolos novos foram desenvolvidos para os acoplamentos Suzuki-Miyaura (ASM) catalisados por níquel e que dispensam o uso de base e de ligante.¹

Apresentamos aqui possíveis avaliações mecanísticas, envolvendo ciclos catalíticos de camada fechada Ni(0)/Ni(II), para o sistema descrito por Bhojane e colaboradores,² que dispensa o uso de base e ligante e utiliza glicerol como solvente, em um ASM entre um sal de arenodiazônio (**1**) e um ácido arilborônico não substituído (**2**), utilizando o próprio solvente como ligante, **L₁** (Figura 1).

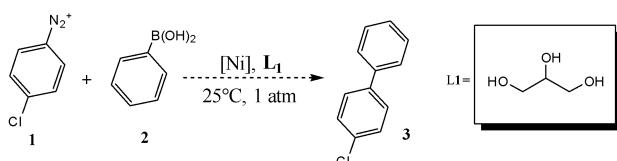


Figura 1. Reação modelo usada nos estudos computacionais.

Metodologia

Geometrias dos reagentes, estados de transição, intermediários e produtos otimizadas à nível DFT/SMD-M06L. Átomos descritos com o conjunto de base *standard* 6-31+G(d,p) para átomos leves e o pseudopotencial relativístico SDD, com o conjunto de funções de bases associado, para o átomo de níquel. Energias livres de Gibbs relativas expressas em kcal.mol⁻¹. Cálculos realizados no pacote Gaussian 09 versão D.01.

Resultados

A etapa de transmetalização (TM) se mostrou a mais energética nos caminhos de reação estudados; o solvente coordenado ao centro metálico atua na estabilização do grupo $-B(OH)_2^+$, proveniente do ácido arilborônico, no estado de transição, com uma barreira aparente, calculada pelo modelo do *span* de energia,³ de 36,1 kcal.mol⁻¹, o que tornaria esse caminho pouco viável. No entanto, os cálculos teóricos mostram que, quando o grupo hidroxila do

solvente é desprotonado, a barreira aparente cai expressivamente para 20,5 kcal.mol⁻¹.

É importante destacar que os autores também realizaram a reação utilizando DMSO como solvente, obtendo rendimentos similares aos em glicerol. Utilizando DMSO como ligante, a barreira aparente obtida para o ciclo é de 29,8 kcal.mol⁻¹. Adicionalmente, se obteve um mecanismo reacional no qual o DMSO atua como base desprotonando o ligante glicerol, **L₁**, levando a uma TOF (*turnover frequency*) de ordem de grandeza comparável à obtida experimentalmente: $TOF_{teórica} = 4.74\text{ }h^{-1}$; $TOF_{experimental} = 0.36\text{ }h^{-1}$.

Conclusões

Os resultados da etapa de TM mostram que o ciclo singuleto pode ocorrer em DMSO, mas só ocorreria em glicerol se o solvente puder ser desprotonado, o que indica que alguma espécie no próprio meio reacional deve estar atuando como base.

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Calculus of the Second Virial Coefficient of Diatomic Molecules

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Palavras-Chave: Second Virial Coefficient, Diatomic Molecules, Potential Energy Surface.

Introduction

The second virial coefficient is related to the equation of state of a real gas¹:

$$\frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m} + \dots$$

where P is the pressure, V_m is the molar volume, R is the ideal gas constant, and $B(T)$ is the second virial coefficient. Knowing $B(T)$ means it is possible to determine the thermodynamic behavior of a real gas. The classical second virial coefficient for is given by¹:

$$B_{cl} = -2\pi N_a \int_0^{\infty} \left[e^{\left(\frac{V(r)}{kT}\right)} - 1 \right] r^2 dr$$

where $V(r)$ is the potential energy in function of r , T is the temperature, N_a is Avogadro's number and k is Boltzmann constant. The real value of $B(T)$ considers the quantum corrections, leading to²:

$$B(T) = B_{cl} + B_1^r + B_1^{a,I} + B_1^{a,\mu} + B_{II}^r + \dots$$

with $B_1^r, B_1^{a,I}, B_1^{a,\mu}, B_{II}^r$ being the quantum corrections. The goal of this work is to obtain the value of the second virial coefficient through a computational program in Python.

Methods

An extensive quantum chemical study of the potential energy surface (PES) of diatomic molecules (H_2 , O_2 , F_2 , CO , N_2 , and NO) was made. We used Gaussian, Columbus, and Molpro programs to calculate a set of ab initio points at CCSD(T)/aug-cc-pVTZ and MRCI/aug-cc-pVTZ. The ab initio points were fitted using the generalized fifth degree Rydberg function and used as the input data to the Python program. The program generates the PES curves and calculates the second virial coefficients. It also plots

the calculated $B(T)$ as lines and the reference data as circles in the same graph.

Results

When running the Python program, a window opens and requests the user to select an input file, containing the information necessary to perform the calculation. After that, the user determines which diatom is going to be studied. That leads to the reference data that is already implemented in the code. At this point, the program performs all the necessary calculus and returns the graphs as shown in Figure 1. It is also possible to download those and save the calculated values of $B(T)$.

Figure 1(a) shows the second virial coefficient of H_2 for various temperatures and Figure 1(b) shows the PES for H_2 .

Conclusion

The results show that our program calculates the second virial coefficient computationally in good agreement when compared to the experimental data. We look forward to continue this work with more complex molecules.

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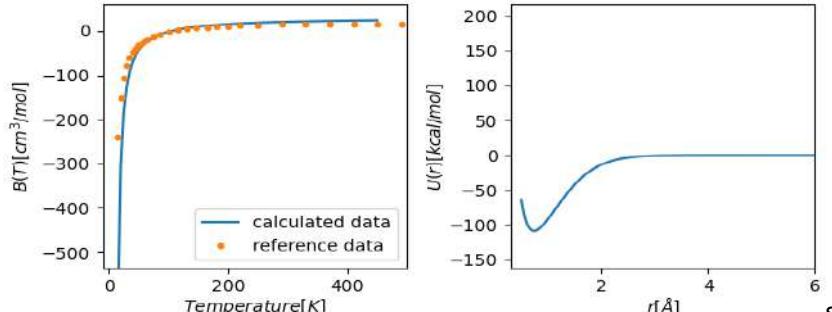


Figure 1: output of the program using MRCI/aug-cc-pVTZ calculated on Molpro.



Aplicação de Métodos de Aprendizagem de Máquina para a descoberta de possíveis inibidores da Chiquimato Quinase de *Mycobacterium tuberculosis* e cálculos de ancoramento molecular

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Palavras-Chave: Aprendizado de Máquina, Chiquimato quinase, tuberculose.

Introdução

O processo de descoberta de novos fármacos é complexo e depende de muitos fatores, dentro desse contexto, técnicas computacionais fornecem métodos rápidos e de baixo custo para encontrar novos protótipos ou candidatos a fármacos[4].

Dentre essas técnicas, a aprendizagem de máquina oferece ferramentas para classificação ou predição de propriedades bastante concisas e robustas[5] e quando combinadas com cálculos de ancoramento molecular podemos encontrar padrões que relacionam determinadas características químicas com sua atividade. Portanto, esse trabalho teve como objetivo aplicar métodos de aprendizagem de máquina para descoberta de possíveis inibidores para Chiquimato Quinase de *Mycobacterium tuberculosis* combinados com cálculos de Ancoramento Molecular.

Metodologia

A base de dados foi constituída por 83271 moléculas obtidas na plataforma Chembank. Foi aplicado duas abordagens de aprendizagem de máquina (AM):

AM não supervisionado: foram extraídas as características químicas das moléculas, sendo elas: átomos aceitores de ligação de hidrogênio, átomos doadores de ligação de hidrogênio e contatos hidrofóbicos. Depois foram submetidas a uma análise de cluster usando o algoritmo DBSCAN, seguido depois por uma análise por similaridade contra três inibidores conhecidos da CQ.

AM supervisionado: Foi utilizado uma rede neural densa adaptado do trabalho de Ekins et. all, 2018. e para o treinamento foram utilizadas 961 moléculas [2, 3]. E os cálculos de ancoramento molecular foram realizados no software Autodock Vina [6], e a estrutura da proteína utilizada foi 2IYQ.

Resultados

Através do método de aprendizagem não supervisionado combinado com a comparação por similaridade foi possível selecionar 90 moléculas do banco de dados, desse grupo 9 compostos obtiveram score no Autodock Vina de -8 até -9.5.

Os resultados obtidos para o modelo de AMS estão de acordo com os dados encontrados na literatura [1]. Os valores de AUC, especificidade e sensibilidade foram, respectivamente: 0,88, 0,84 e 0,77. Apesar do conjunto de treinamento ser pequeno, foi possível obter um modelo com resultados satisfatórios. O classificador encontrou 810 moléculas que poderiam possuir atividade anti-TB. Quando esse conjunto de moléculas foi submetido ao cálculo de ancoramento molecular, foi possível encontrar 50 moléculas cujos score variaram de -9 até -9,8, valores mais negativos que o encontrado para o seu substrato (chiquimato), cujo valor foi de -6,9.

Conclusões

Conclui-se que o modelo de aprendizagem de máquina não supervisionado pode ser uma estratégia interessante quando não dispomos de uma base de dados de treinamento ou poucas moléculas conhecidas. Pois utilizando apenas três inibidores da proteína foi possível encontrar um pequeno conjunto de moléculas que podem apresentar atividade para CQ. Todavia, a segunda estratégia mostrou-se mais eficiente pois o conjunto de propostas químicas foi muito maior, e com valores de score mais interessantes. E esse resultado foi obtido através de um modelo construído utilizando um pequeno conjunto de moléculas (961 compostos) de treinamento, diferente da referência utilizada nessa abordagem, na qual os autores utilizaram um conjunto de 18 mil moléculas aproximadamente. Estudos futuros ainda serão realizados.

Agradecimentos

Agradeço o apoio da CAPES, UFRGS.

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Study of effect of *ortho*- and *para*- chlorine substitution on hydroxychlorochalcone in gas phase using DFT and Car-Parrinello Molecular Dynamics

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Keywords: Modelagem, hidroxiclorochalcona, Dinâmica Molecular de Car-Parrinello.

Introduction

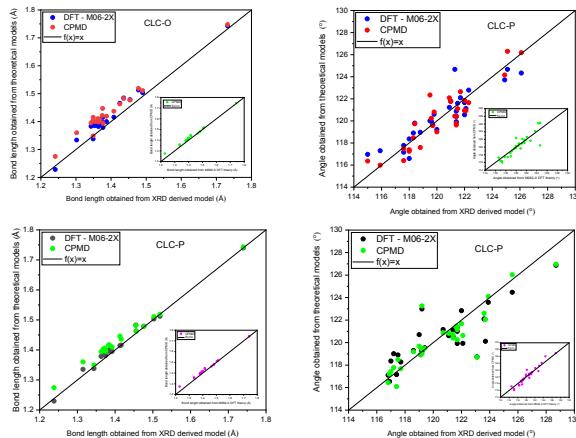
Chalcones and their derivatives are studied due to their simple structural form, versatility and wide range of biological properties with potential applications in the clinical area, such as: anti-inflammatory, antibacterial, antimalarial, antioxidant and others. In addition, several chalcones are reported to demonstrate nonlinear optical properties, generating interest in the field of materials science [1-2]. *Ab initio* Car-Parrinello molecular dynamics uses classical mechanics to describe ionic motion, obtained from solutions to Newton's equations, and quantum mechanics through the Born-Oppenheimer approximation to separate nuclear and electronic coordinates, using formulation of a Car-Parrinello extended lagrangean [6].

Methodology

The theoretical calculations aim to determine the geometric and electronic properties of the substitutions of the chlorine atom in the *ortho* and *para* positions of two hydroxychlorochalcones, in gas phase, using CPMD, and compare the results found with experimental values obtained by Diffraction of X-rays and the Density Functional Theory (DFT). For the calculations use the parameters: cutting energy of 25 Ry for the expansion of the wave functions of the system; temperature was controlled at 300 k using a Nosé-Hoover thermostat; the statistical ensemble used will be the NVT.

Results and discussion

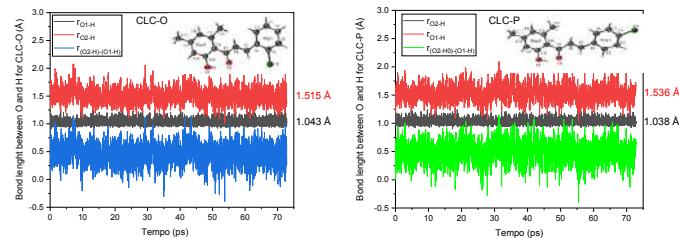
Figure 1 – Comparison between the bond lengths obtained using DFT and CPMD method and experimental result for CLC-O.



There is a good agreement between the values obtained by the theoretical models (DFT – M06-2X

and CPMD) and the experimental data for the two chalcones, as can be seen in Figure 1. The values between the theoretical and experimental results and between the theoretical results approximate the line $f(x)=x$. We highlight the highest values for the relative percent difference in binding distance for the calculations using CPMD compared to the experimental values. For Chalcone CLC-O we have C1-C2 (4,005%), C7-C8 (4,449%), C12-C13 (4,935%) and C15-C10 (5,170%). For the Chalcone CLC-P the biggest differences are present for the lengths C7-C8 (3.433 %) and C15-C10 (3.338 %).

Figure 2 – Time evolution of bonds involved in the intramolecular hydrogen bond CPMD method in the gas phase.



Intramolecular hydrogen bonds were classified according to the geometric parameters proposed by Jeffrey [4]. The CLC-O presented an average length of 1.515 Å and an average angle of 150.9°. The CLC-P presented an average length of 1.536 Å and an average angle of 150.3°. Both intramolecular hydrogen bonds showed moderate intensity, referring to the distance within the range of 1.5 Å to 2.2 Å and angle above 130°.

Conclusion

The good agreement between theoretical and experimental results validates the CPMD method. The position of chlorine in the *ortho* and *para* forms does not affect the H-O1 bond. The effect of Chlorine replacement in chalcones can be amplified, using CPMD, in a solvation study of chalcones.

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COMPUTATIONAL STUDY OF Pt-195 NMR CHEMICAL SHIFT IN Pt(II) COMPLEXES WITH ANTITUMORAL POTENTIAL

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Palavras-Chave: Cancer, Pt(II) complexes, NMR.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy has played a significant role in the design and discovery of new platinum drugs in recent years. Pt-195 NMR is used as a tool in the characterization of new structures, optimization of complex targets and elucidation of reaction mechanisms^{1,2}. The Pt-195 nucleus is the only NMR active isotope of platinum, presenting a wide range of values in NMR spectroscopy, from +8000 ppm to -7000 ppm, relative to the reference compound, $[\text{PtCl}_6]^{2-}$ in D_2O ¹. The computational prediction of the Pt-195 NMR chemical shift is influenced by factors such as electronic correlation, basis sets, solvent and relativistic effects^{1,2}. In a previous paper, Paschoal and collaborators¹ proposed a computational protocol for predicting the Pt-195 NMR chemical shift, which was tested on a set of 258 distinct Pt(II) complexes, presenting an average relative deviation of only 5%. So, in the present study, we applied the computational protocol proposed in this previous paper¹ in a set of 101 distinct Pt(II) complexes.

Methodology

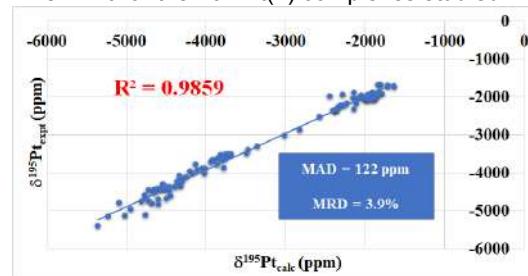
A set of 101 distinct Pt(II) complexes with available experimental data for Pt-195 NMR chemical shift were selected. The structure of the complexes were optimized and characterized as a minimum point on the potential energy surface through harmonic frequency calculations at B3LYP/LANL2DZ/def2-SVP/IEF-PCM(UFF) level and the Pt-195 NMR chemical shift ($\delta^{195}\text{Pt}$) were obtained from the equation: $\delta^{195}\text{Pt}_{\text{calc}} = -0.9250 \times ^{195}\sigma_{\text{calc}} - 2065.7558$, where the shielding constant (σ) was calculated at the GIAO-PBE/NMR-DKH/IEF-PCM(UFF) level¹. All these calculations were performed in the GAUSSIAN 09 Rev. D.01 program.

Results and Discussion

From the calculated results (Fig. 1), it can be observed an excellent correlation between calculated and experimental Pt-195 NMR chemical shift, with a $R^2=0.9859$. Besides, the mean absolute deviation (MAD) and the mean relative deviation (MRD),

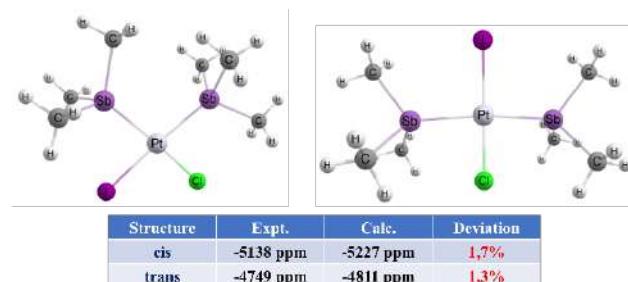
considering the 101 Pt(II) complexes, were only of 122 ppm and 3.9%, respectively.

Fig. 1. Correlation between calculated and experimental $\delta^{195}\text{Pt}$ for the 101 Pt(II) complexes studied.



Finally, from Fig. 2 it can be seen that the proposed computational model can even be used to distinguish *cis* and *trans* isomers.

Fig. 2. $\delta^{195}\text{Pt}$ calculated for *cis*- and *trans*- $[\text{Pt}(\text{Sb}(\text{CH}_3)_3\text{Cl})]$



Conclusions

The study presented the application of a computational protocol for predicting $\delta^{195}\text{Pt}$ in Pt(II) complexes. The calculated results for a set of 101 complexes showed that the used model used, with a MRD of only 3.9%, is an excellent alternative for the study of NMR properties in Pt complexes.

Acknowledgments

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Quantum Chemistry study of the Pt(II,IV) complexes structures with anticancer activity.

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Keywords: MMFF94, Platinum, DockThor, force field parametrization.

MMFF94¹ is a force field developed by Merck, mainly used in molecular mechanics calculations such as molecular Docking for biological systems. Parameters for the Platinum (Pt) atom are available only for some programs^{2,3}, but they are restricted and commercial. In this context, DockThor⁴ is a free web server for docking, and it uses a scoring function based on MMFF94, but lacks parameters for this atom and having such data would help the development of research in these antineoplastic Pt group. The main difficulty in derived force field for metals like Pt, is the behavior of metallic center which is not transferable in all cases, Ex. Pt complexes with biological targets like the next figure⁵:

Molecular geometry of 22 derivatives coordination complexes for Pt(II, IV) were fully optimized, named PLA_N°. We used DFT

Minnesota functional meta-GGA M06L and triple split basis set polarization Kalsruhe (for H, N, Cl atoms) with relativistic correction ZORA and SARC as the level of theory for Pt atom⁶, well validated with a simple basis set SVP and TZVPP for Cisplatin (prototype of this family). All the calculations were performed in gas phase with Orca⁸ 4.2.1 package, using the SDumont supercomputer from LNCC⁷ (Brasil) facilities. The optimized structures were confirmed by vibrational analysis with no negative eigenvalues. All the structures and post-processing analysis were performed by using Avogadro and Chemcraft packages.

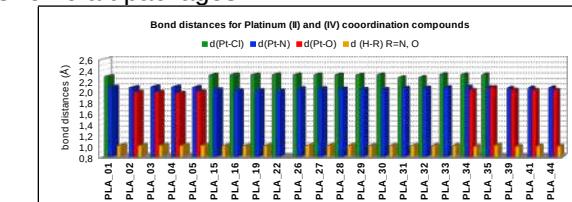


Figure 1: Calculated bonds distances for the Pt (II, IV) complexes.

Fig. 1 shows the main bond distances for all Pt complexes studied. The d(Pt-Cl) bond was the longest (> 2,294 Å) one, and it represents 68% of the total bonds in the compounds. The d(Pt-N) bonds are in all structures, and they are smaller than the previous one. The d(Pt-O) bond is the less common (40% total), and presented the shortest

bond length (> 1,97 Å). We considered d(H-R) bond, being R=N, O, the narrowest one (< 1,024 Å), and it presents 95% of total. Order: d(Pt-Cl) > d(Pt-N) > d(Pt-O) > d(H-R).

Each bond distance was analyzed more closely and grouped according to the type of the atom (table 1), which includes the H atoms co-planar in H-N-Pt-R (R=O, Cl) of NH₃ ligands. The angles did not behave in the same sense as the bond distances, and they presented larger standard deviations.

Table 1: Optimized bond distances and bond angles for all Pt complexes.

ALL GEOMETRIES			SQUARE-PLANAR GEOMETRIES			
type	average (Å)	standard deviation	N	type	average (Å)	
d(Pt-Cl)	2.314314	0.015	8	d(Pt-Cl)	2.301783	0.010
Pt - Cl (cis dicloro)	2.35207	0.030	19	Pt - Cl (cis dicloro)	2.352057	0.003
Pt - Cl (trans dicloro)	2.346235	0.000	2	Pt - Cl (trans dicloro)	2.374630	0.002
Pt - Cl (monocloro)	2.274820	0.002	2	Pt - N without subdivided	2.318770	0.014
d(Pt-N)			d(Pt-N)			
Pt - N (like NH ₃)	2.078260	0.024	20	Pt - N (like NH ₃)	2.083758	0.005
Pt - N (like NH ₂)	2.082574	0.019	19	Pt - N (like NH ₂)	2.075547	0.031
Pt - N (aromatic)	2.023663	0.009	6	Pt - N (aromatic)	2.023663	0.009
Pt - N (like NH)	2.002030	-	1	Pt - N (like NH)	2.002030	1
Pt - N (azide)	2.020207	0.032	6	Pt - N without subdivided	2.070280	0.030
d(H-R)			d(H-R)			
H - N (like HSN)	1.015904	0.003	60	H - R	1.014254	0.001
dPtO			dPtO			
Pt - O (dicarbonyl cycle)	2.007284	0.024	7	Plane - R	1.018493	0.002
Pt - O (linear O-C-O)	2.089085	0.019	2	Plane - R	1.015581	0.002
Pt - O (monocarbonyl cycle)	1.970280	-	1	all without subdivided		
Pt - O (like OH)	2.070653	0.032	6	all without subdivided		
$\angle(Cl-Pt-Cl)$			$\angle(N-Pt-N)$			
average	92,975	92,192	92,165	89,160	87,643	
standard deviation	2,430	6,749	6,072	2,743	2,966	
N total angles	8	24	4	52	40	
Number of structures	4	11	4	15	11	
$\angle(O-Pt-O)$			$\angle(N-Pt-O)$			
$\angle(Cl-Pt-O)$			$\angle(N-Pt-O)$			

Conclusions: All results lead to the determination of d(Pt-Cl) and $\angle(Cl-Pt-Cl)$ as the metallic core-ligand bond and angle more uniform and less dispersed. For a couple of optimized structures there are experimental or theoretical data available, while for others were not found. In general, our results are in good agreement with the available data^{9,10,11}. Beyond these results, atomic partial charges and vibrational modes, electric properties such as dipole moment and polarizability were also calculated to derive the force field average parameters for the Pt atom. It will be applied in future Docking studies using DockThor package.

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Sponsors:



Theoretical study of the formation of inclusion complexes between a set of flavonoids and β -cyclodextrins, pure and modified

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Keywords: SARS-CoV-2, flavonoids, beta-cyclodextrin, inclusion complexes.

INTRODUCTION: Flavonoids (FLVs) are natural species that have different biological and pharmacological activities, representing potential antiviral, antibacterial, anti-inflammatory active principles.¹ Recent studies have been shown that flavonoids can act to prevent SARS-CoV-2 through inhibition of human host cell enzymes, such as furin and transmembrane serine protease II (TMPRSS2), which are fundamental in the viral infection process.² However, most flavonoids have low water solubility, limiting their oral administration, bioavailability and, consequently, their effectiveness as an active principle. One of the strategies to solve this problem is the formation of inclusion complexes between flavonoids and cyclodextrins (CDs). CDs are conical cyclic maltooligosaccharides, capable of solubilizing in aqueous media and encapsulating hydrophobic molecules inside their cavity.³ Therefore, CDs are able to sequester cholesterol molecules, disrupting the viral envelope of SARS-CoV-2. The adhesion between the viral envelope and cell membrane cholesterol is essential for the successful entry of the coronavirus.⁴ Inclusion complexes between β -CD and flavonoids have been explored as potential additives for nasal irrigation in the prevention of COVID-19, without toxic effects.⁵ Thus, the work presented here aims to investigate the stability of inclusion complexes between flavonoids and CDs, pure and modified, in gas phase and in aqueous medium, making use of the density functional theory (DFT) associated with the tight-binding approximation (DFTB).

METHODOLOGY: As a first step, the β -CDs and Methyl- β -CDs monomers were constructed from experimental data found in literature. Initially, three FLVs, quercetin (QRT), herbacetin (HBT) and luteolin (LUT), Fig. 1, were chosen to formation of FLVs/CDs complexes.

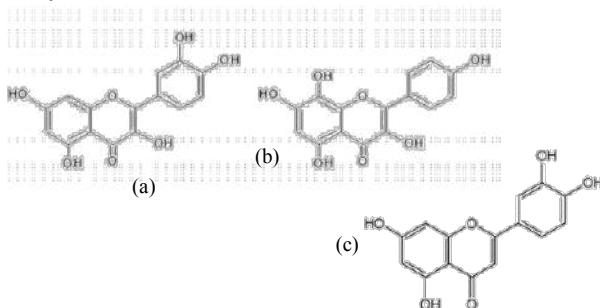


Fig. 1: QRT (a), HBT (b) and LUT (c) flavonoids.

The FLVs structures were perpendicular approximated to CDs monomers, starting from 5.0 Å of the hydrophobic center of the CD monomer. The optimization of FLV/CD was first performed with the DFTB method, and their coordinates were used as starting point to DFT calculation. In the DFT step, the calculations were done using B3LYP/6-31G(d,p) methodology. As second step, the optimized complexes were submitted to Self-Consistent Reaction Field (SCRF) calculation using SMD keyword; Truhlar's and coworker's solvation model, recommended by Gaussian as preferred one to calculate ΔG_{solv} . All structures were confirmed to be minimum energy conformations by frequency calculation. The complexation energy was calculated using counterpoise method to perform BSSE.

RESULTS: The calculated complexation energy (E_{cp}) for the FLVs/ β CD complexes follows the increasing order: HBT<QRT<LUT, with values of 4.9, 7.1 and 9.5 kcal mol⁻¹, respectively. The number of intermolecular H-bonds produced into of each complex is: QRT=4, HBT=4 and LUT=2.

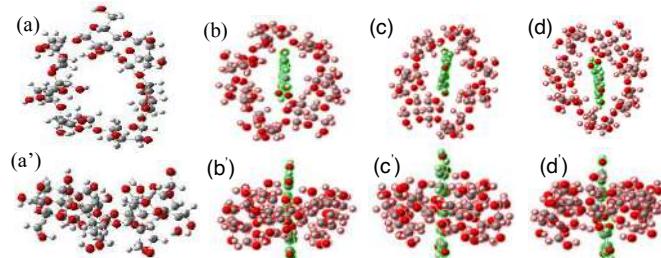


Fig. 2. Superior and ('') lateral view: isolated β -CD (a) and FLV/CD complexes quercetin (b), herbacetin (c) and luteolin (d); all optimized at B3LYP/6-31G(d,p) level.

When the complexes are submitted to water implicit solvation through IEFPCM model, the calculated ΔG_{solv} is: -109.0, -110.0 and -112.8 kcal mol⁻¹, for QRT, LUT and HBT, respectively. The DFT calculations using the Methyl- β -CD are already in progress.

CONCLUSIONS: Among the FLVs/ β -CD complexes tested, the β -CD/LUT present highest stability. However, the small values found to E_{cp} indicate the need of using modified CDs.

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Computational study of the reduction mechanisms of platinum (IV) to platinum (II) compounds in gas phase.

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Keywords: platinum, Pt (IV), gas phase

Introduction

Pt(IV) compounds have been studied and appear to be interested in developing therapies against cancer to minimize the side effects of cisplatin, besides expanding its therapeutic effect for other types of cancer¹. Several studies are using cisplatin-like compounds in the literature, but what happens in the reduction reaction of these compounds is still a mystery¹. Two prodrugs of Pt (IV) will be the objects of study of this work. The molecular structures of these two compounds are showing in Figure 1.

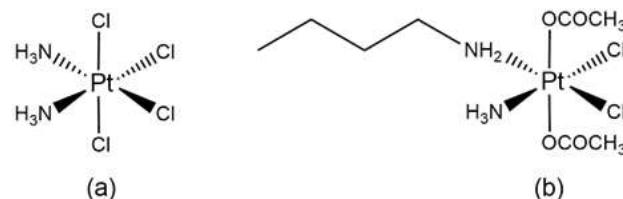


Figure 1: Molecular structures of (a) cis-diaminotetrachloroplatin(IV) (CDT-IV) and (b) bis(acetate)amino(n-butylamino)dichloroplatin(IV) (NBA-IV).

Still essential to study the process of reducing these compounds in the body. Because studies report that for these prodrugs to present pharmacological action, they must undergo a previous reduction², and we need a better description of the intrinsic mechanism.

Methodology

All calculations were performed using Gaussian 09 software. Optimization, vibrational analysis, and molecular orbitals calculations were performed for both molecules varying total charges in 0, -1, and -2 in order to simulate the different oxidation states of platinum +4, +3, and +2, respectively. *Ab Initio* and DFT calculation was using, respectively, MP2 and M06-2x functional, and using 6-31g(d,p) for light atoms and lanl2dz ECP for platinum.

Results

In the optimization and frequency calculations, similar structural changes were observed for the two molecules when modifying their total charges, regard primarily to the release of the ligands. The elongation of the axial bonds in both molecules is evident for the two methods used, as shown in Figure 2:

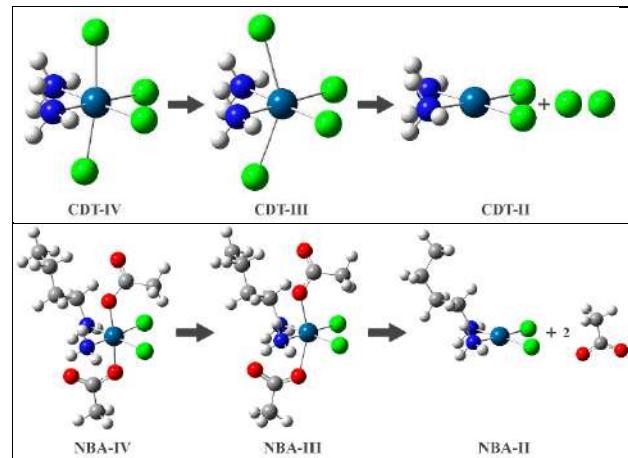


Figure 2: Structural representation of the reduction process of the two species.

For both methods with Pt(IV), Pt(III), and Pt(II), the axial bonds are elongated with an average of 2.3, 2.7, and >4 Å, respectively. The bond angles are close to 90°(± 10), and the dihedral angles remain zero in all cases, suggesting that the Pt(IV) compound has octahedral geometry and the Pt(II) compound has a plane quadratic geometry. Furthermore, for the CDT-III compound, we have found a negative frequency of -54.88 cm⁻¹ (at M06-2x), which may indicate a transition state. Still, such processes are thermodynamically favorable, presenting $\Delta G = -58.9$ kcal/mol and $\Delta G = -47.8$ kcal/mol, respectively, by the MP2 method. NBO/MP2 for CDT-IV indicate d_{z^2} as LUMO, assuming so, the release of the axial ligands. For the NBA-IV tough, the LUMO symmetry is $d_{x^2-y^2}$, and it suggests that a different mechanism, from the one presented in Fig.2, could occur for Pt(IV) complexes reduction.

Conclusions

It is possible to assume a favorable reduction process. The IRC calculations are being carried out to verify the maximum founded. We are also checking other structures for Pt(II) products and their interconversion using solvent approaches.

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Computational exploration of the degradation of chemical warfare agents by the UiO-66_NH₂ MOF

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Keywords: *Chemical Warfare Agents, DFT, Metal-Organic Frameworks.*

INTRODUCTION

Metal-organic frameworks (MOFs) owing to their unique features in terms of high surface area/pore volume and large concentration of active sites are an appealing platform of porous materials for the capture and degradation of chemical warfare agents (CWAs)¹. Zr-MOFs are known to be active for capturing CWAs and even catalyzing their hydrolysis. Among them, UiO-66_NH₂ has been revealed as one of the most efficient catalysts although the microscopic mechanism is yet to be fully understood. We explored the catalytic degradation performances of OA-UiO-66_NH₂ for both real nerve (GD and VX) and blister (HD) agents. The degradation mechanisms for all CWAs were carried out using Density Functional Theory (DFT).

METHODOLOGY

DFT calculations were performed using Quantum-Espresso package under periodic boundary conditions and plane wave functions as basis set². UiO-66_NH₂ was first fully DFT-geometry optimized in the presence of 1 molecule of GD, HD and VX. The climbing-image nudged elastic band method³ was used to determine the minimum energy paths (MEP) for the degradation reaction of all CWAs.

RESULTS

Gas chromatograph measurements revealed GD had a half-life shorter than 4 minutes and it is converted to more than 90% within 1.6 hours and 98% after 3 hours. In case of VX, the half-life is 6 minutes, and this CWA is converted to more than 90% within 1.3 hours and 96.2% after 3 hours. HD can be hydrolyzed in water/ethanol mixture solvent without the need of a catalyst. In the presence of OA-UiO-66_NH₂, the reaction rate is more than 2 times faster and HD has a half-life lower than 90 minutes, and more than 85% of HD is decomposed after 340 minutes. The degradation mechanism of VX is reported in Figure 1. During the first step of the reaction, VX interacts with the terminal -OH group of the MOFs via its phosphorus atom while the water coordinated towards Zr interacts with the sulfur atom. As the reaction proceeds the distance between the CWA molecule and the MOF atoms becomes shorter leading to the coordination of the -OH group to the VX and to a strong interaction of the sulfur atom with the

hydrogen atom of the coordinate water (1.89 Å), as indicated in the TS (Figure 1b). The next reaction step is the decomposition of the VX via the breaking of the bond P-S with a subsequent migration of the hydrogen atom from the coordinated H₂O to the sulfur atom where the ethyl methylphosphonic acid (EMPA) and (2-diisopropylamino)ethanethiol (DESH) molecules are formed (Figure 1c). The desorption energy of EMPA and DESH from the product is low (45.6 kJ mol⁻¹) and the MEP of the corresponding degradation mechanism implies a moderate activation energy barrier of 168.7 kJ mol⁻¹.

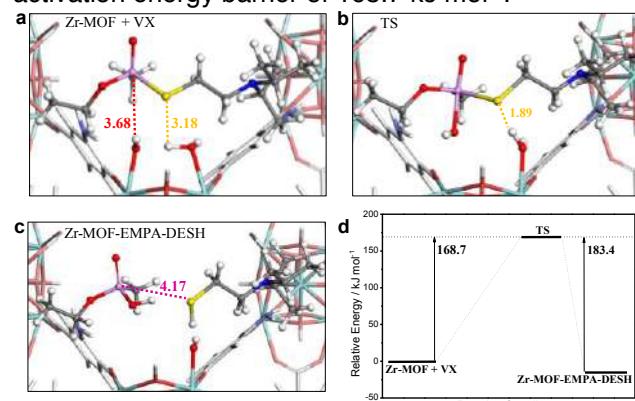


Figure 1: Hydrolysis degradation mechanism of VX by UiO-66_NH₂. (a) Reactant, (b) Transition state, (c) Product and (d) simulated MEP.

CONCLUSIONS

The OA-UiO-66_NH₂/PAN fibrous mats unraveled to enable multi-degradation of GD, HD and VX by hydrolysis reaction. The hydrolysis rate was shown to be more than 3 times faster for HD than without catalyst and the hydrolysis conversion of GD and VX was shown to be close to 100% after 3 hours. Importantly, the degradation mechanisms of all CWAs were elucidated using DFT calculations. The associated energy barriers and the desorption energy of the degraded products support that UiO-66_NH₂ is a promising catalyst.

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Estudo teórico comparativo de propriedades eletrônicas e termodinâmicas de parabenos que mimetizam o 17 β -estradiol.

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Palavras-Chave: DFT, parabenos, disruptores endócrinos.

1. Introdução

Moléculas com ação estrogênica são capazes de se ligar ao receptor de estrogênio β e alterar processos hormonais naturais¹. Estudos sobre a relação estrutura-atividade destes disruptores endócrinos consideram que alguns dos fatores essenciais para a interação com a enzima são:
(a) a presença de um anel fenólico;
(b) presença de centros hidrofóbicos na estrutura². Parabenos (figura 1), ésteres do ácido p-hidroxibenzoico, mostraram ser capazes de se ligar ao receptor do hormônio 17 β -estradiol em testes *in vitro*.

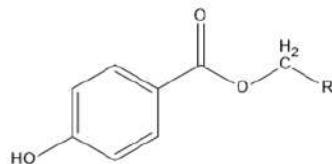


Figura 1. Estrutura dos parabenos.

No presente trabalho, a fim de complementar resultados experimentais pré-existentes sobre a estrogenicidade destas moléculas, realiza-se uma análise comparativa de propriedades eletrônicas e termodinâmicas de alguns parabenos, seus metabólitos principais e o 17 β -estradiol.

2. Metodologia

Os cálculos foram realizados com o auxílio do software Gaussian 09. As estruturas estudadas foram: metil (MPB), propil (PPB) e butilparabeno (BPB), ácido p-hidroxibenzoico, metanol, propanol, butanol e estradiol. Os seguintes cálculos foram realizados:

- otimização da geometria das estruturas;
- cálculo de cargas parciais, via método de população eletrônica (NBO);
- simetria dos orbitais de fronteira;
- a estabilidade em água e n-octanol, via solvatação implícita (IEPCM);
- Análise da variação das funções termodinâmicas na reação de metabolização.

Todos os cálculos realizados utilizaram o método DFT com B3LYP/ 6-31g(d,p).

3. Resultados

Há grandes diferenças estruturais entre as moléculas estudadas e o estradiol, sendo a maior delas a inexistência de um segundo grupo doador de ligação de H. Entretanto, nos parabenos e no

derivado ácido, a presença de um anel fenólico é uma similaridade estrutural essencial. Este grupo permite a interação com a enzima receptora via específicas ligações de H com resíduos de aminoácidos ali presentes.

Além disso, a presença de um fenol nas estruturas faz com que os orbitais HOMO e LUMO destas moléculas possuam simetria e diferença energética similares as do hormônio, de modo a indicar uma possível reatividade química semelhante.

A metabolização dos parabenos se dá via uma reação de hidrólise catalisada por esterase. Na tabela 1 observa-se os valores obtidos após o cálculo da variação das funções de estado. Nota-se um baixo valor de entalpia e um valor negativo de entropia. Isto indica que está é uma reação termodinamicamente não favorável sem a presença de uma enzima. Além disso, não se obteve valores congruentes de energia livre de Gibbs, sendo estes próximos à incerteza química e um indicativo da diminuição da robustez do método computacional escolhido.

Tabela 1. Funções termodinâmicas reacionais, utilizando água como solvente implícito.

Estrutura	ΔG (kcal/mol)	ΔH (kcal/mol)	$-T\Delta S$ (cal/mol/K)
MPB	0,69	1,63	-0,94
PPB	0,36	1,55	-1,18
BPB	-0,29	1,19	-1,48

4. Conclusão

Após a análise de propriedades químicas básicas entre as estruturas estudadas, conclui-se que uma das similaridades mais importantes mostrou-se ser a presença de um anel fenólico. Além disso, observou-se a necessidade do uso de parâmetros computacionais que simulem melhor o meio reacional. A inclusão de resíduos de aminoácidos da enzima catalisadora e o estudo do estado de transição desta metabolização também são pontos importantes a serem adicionados.

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Efeito da dopagem do íon fluoreto no bandgap da perovskita $\text{CH}_3\text{NH}_3\text{PbI}_3$

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Palavras-Chave: perovskita, $(\text{CH}_3\text{NH}_3)\text{PbI}_3$, dopagem, flúor.

INTRODUÇÃO

Perovskita é o nome dado à classe de materiais com estrutura cristalina de fórmula geral ABX_3 , onde A é um cátion, de raio geralmente maior que o outro cátion B , e X é um ânion. A rede cristalina é formada por arranjos octaédricos BX_6 permeados pelo cátion A . A aplicação mais popular das perovskitas são nas células solares, nas quais são usadas como camada ativa de conversão de luz em energia elétrica. Em 2009 foram construídas as primeiras células solares de perovskita, com eficiência de 3%, hoje ela é superior à 26%.¹ Uma das perovskitas mais conhecidas e que apresenta bom desempenho, é a $(\text{CH}_3\text{NH}_3)\text{PbI}_3$. Apesar do grande potencial em conversão de energia, o problema que a impede de uma aplicação em grande escala é sua instabilidade estrutural. Ao ser exposta à humidade, calor, oxigênio, luz ou ainda à combinação destes fatores, a perovskita se degrada rapidamente perdendo sua habilidade em conversão de luz em energia elétrica. Para ser uma tecnologia competitiva com os painéis à base de silício, os mais comuns, as células de perovskita precisam ter durabilidade em torno de 25 anos, algo que ainda está longe de ser alcançado.² Assim, é de suma importância o aumento da estabilidade intrínseca da estrutura cristalina da perovskita para sua futura comercialização. Fu et. Al, introduziram o íon fluoreto na perovskita inorgânica $\text{CsPbBr}_{2-x}\text{F}_x$ e conseguiram ganho na eficiência de conversão fotoelétrica e, principalmente, na estabilidade contra humidade, em relação à perovskita precursora. Esse ganho foi obtido até certa concentração de dopagem, até que o tamanho dos grãos caiu drasticamente e o bandgap cresceu.³ Assim, o objetivo deste trabalho é entender como o íon fluoreto altera as propriedades estruturais e eletrônicas dos cristais de perovskita, uma vez que essas informações ainda são muito escassas na literatura.

METODOLOGIA

Utilizamos uma metodologia baseada na teoria do funcional da densidade dentro da aproximação GGA com funcional de troca-correlação PBE, com pseudopotencial USPP e correção de dispersão D3, implementados no pacote Quantum-Expresso. Inicialmente foi feita a otimização da geometria e em seguida o cálculo de estrutura de bandas da célula unitária tetragonal (geometria encontrada à temperatura ambiente) da $(\text{CH}_3\text{NH}_3)\text{PbI}_3$, com 48 átomos. E depois a otimização e a estrutura de bandas da perovskita dopada com ânion fluoreto, $(\text{CH}_3\text{NH}_3)\text{Pb}(\text{I}_x\text{F}_{1-x})_3$, com $x=0,9$ e $x=0,8$.

RESULTADOS

O bandgap encontrado para a perovskita pura, 1,554 eV, o que foi muito próximo do relatado na literatura, de 1,594 eV.⁴ Mesmo em pequena quantidade, o flúor distorce a célula unitária de tal forma, que perde sua geometria tetragonal e passa a ser triclinica. Com o aumento da

concentração de íon fluoreto, 0,1 e 0,2, o bandgap aumentou para 1,71 eV e 2,01 eV, respectivamente.

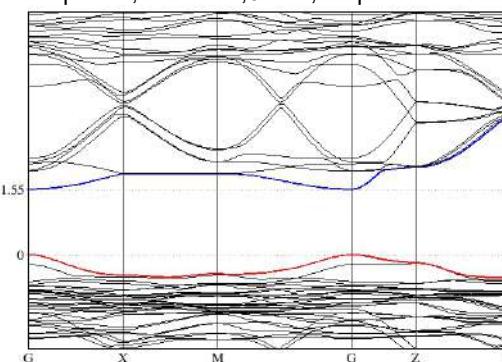


Fig. 1. Estrutura de bandas da $(\text{CH}_3\text{NH}_3)\text{PbI}_3$.

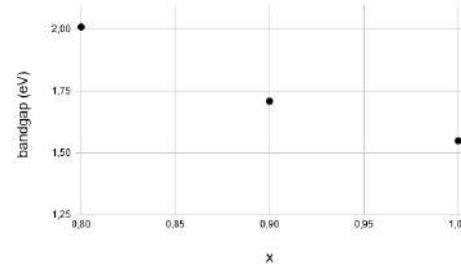


Fig. 2. Bandgap encontrado para $(\text{CH}_3\text{NH}_3)\text{Pb}(\text{I}_x\text{F}_{1-x})_3$, com $x=1,0$; 0,9; 0,8.

CONCLUSÕES

Com a inclusão do F houve aumento do bandgap, o que se deve ao fato da alta eletronegatividade do flúor.⁵ Mas foi surpreendente o fato de haver um aumento tão grande mesmo com uma concentração tão baixa de fluoreto. Dessa maneira, pretende-se ainda fazer cálculos estruturais (como bulk modulus) para saber se há correlação da dureza com abertura do bandgap, além de explorar outras formas de utilizar a alta eletronegatividade do F, a favor do aumento de estabilidade da perovskita na célula solar.

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MODELAGEM COMPUTACIONAL DE PROPRIEDADES LUMINESCENTES DE NOVOS COMPLEXOS DE Eu(III) COM LIGANTES CARBOXILATOS

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Palavras-Chave: Carboxilato, Lantanídeo, JOYSpectra.

INTRODUÇÃO

Complexos de lantanídeos(III) apresentam propriedades luminescentes favoráveis a uma grande variedade de aplicações ópticas, devido a emissão quase monocromática e longos tempos de vida de emissão.¹ Dessa forma, o design teórico de propriedades fotofísicas desses complexos torna-se um desafio. Este trabalho apresenta um estudo teórico e experimental de complexos de Eu(III) contendo o ligante acrilato (E)-3-(tiofen-3-il) para a compreensão dos processos de luminescência.

METODOLOGIA

Os complexos formados por unidade(s) do tipo $[Ln(ATA)_3H_2O]$, em que $Ln = Eu, Gd$, e ATA = acrilato (E)-3-(tiofen-3-il), (Ln -ATA) foram sintetizados e caracterizados. As estruturas propostas foram otimizadas com o funcional B3LYP e as energias dos estados excitados singuleto e triplo foram obtidas por TD-DFT com o funcional CAM-B3LYP. Todos os cálculos empregaram os conjuntos de funções de base 6-31G para átomos de C e H, 6-31+G para O e S, e os íons trivalentes de Eu(III) foram descritos pelo conjunto de funções de base e pseudopotencial de caroço efetivo relativístico MWB52, que inclui os elétrons 4f no caroço. Para a modelagem das propriedades luminescentes, foram realizados cálculos dos parâmetros de intensidade utilizando o modelo de polarizabilidade do recobrimento da ligação química, implementado na plataforma web JOYSpectra.²

RESULTADOS E DISCUSSÃO

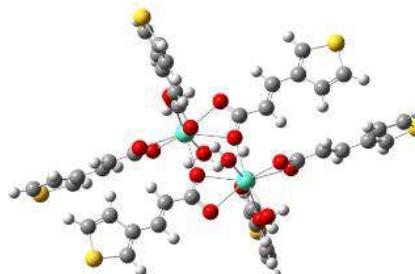
Através do modelo estrutural binuclear do complexo de Eu(III) proposto foi possível observar alta concordância entre as propriedades fotofísicas da teoria com o experimento. A estrutura binuclear é formada por dois ligantes em ponte que se coordenam de forma bidentada a um centro metálico e interagem com o outro centro mantendo a distância entre os dois íons (Eu-Eu) de 4,16 Å. Dois ligantes ATA e duas moléculas de água completam a esfera de coordenação de cada íon Eu(III) da estrutura proposta. Além disso, a estrutura apresenta uma assimetria pronunciada na coordenação dos ligantes-ponte em torno dos íons Eu(III) (Figura 1). O funcional B3LYP forneceu valores de distâncias de ligação de acordo com às obtidas para complexos similares. A partir dessa estrutura foram obtidas as

energias dos estados excitados triploto e singuleto, as quais estão em boa concordância com os valores obtidos experimentalmente. Os valores Ω_2 e Ω_4 foram obtidos a partir de várias abordagens, uma vez que não há registro da utilização da plataforma para complexos binucleares: considerando apenas o poliedro de coordenação de um dos sítios (1), excluindo o segundo íon Eu(III) da lista de átomos do complexo binuclear, e excluindo-se o primeiro íon Eu(III) da lista (3). Na Tabela 1 são apresentados os parâmetros de intensidades experimentais e teóricos calculados.

Tabela 1: Valores dos parâmetros de intensidade (10^{-20} cm^2).

Eu-ATA	Ω_2	Ω_4	Ω_6
Experimental	9,40	7,68	-
Mononuclear	16,58	4,03	2,28
Binuclear (1)	9,39	7,68	1,71
Binuclear (2)	9,39	7,68	1,3
Binuclear (3)	9,39	7,68	1,66

Figura 1: Estrutura otimizada: complexo binuclear



CONCLUSÕES

A estrutura binuclear do complexo Eu-ATA forneceu valores de propriedades eletrônicas e dos parâmetros de intensidade em concordância aos valores experimentais. A partir das taxas de transferência de energia calculadas e estimadas está sendo proposto um diagrama de transferência de energia adequado para a previsão do tempo de vida e rendimento quântico desse sistema. Esses resultados bem como caracterizações adicionais poderão auxiliar na elucidação estrutural e do processo de luminescência de complexos de Eu(III).

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XXI SBQT

Computational studies of dopamine in aqueous solution

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Introduction

Dopamine ($C_8H_{10}O_2NH_2$) is a neurotransmitter associated with cognitive, sensory, psychic, and motor activities¹. It is found predominantly in the brain and the cationic form at blood pH². Many studies point to its uneven conformational balance due to intramolecular interactions between the amine and catechol groups that stabilize the gauche conformation, making it competitive in energy with the trans conformation². The studied conformational structures are showing in Figure 1.

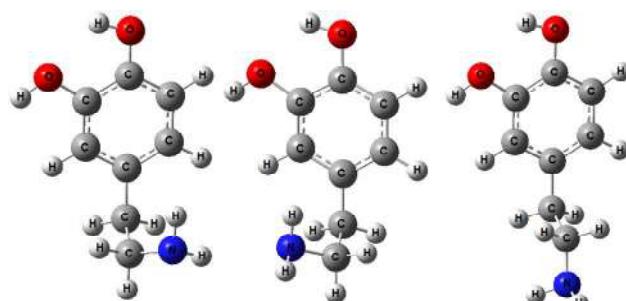


Figure 1: Molecular structures of gauche distal-perpendicular, gauche proximal-perpendicular, and trans-perpendicular, respectively

It is of great interest to describe the thermodynamic differences between structures regarding their interactions with water and intermolecular interactions when there is a solvent effect.

Methodology

For both neutral and cationic forms on these conformational shapes, optimization of geometries, vibrational frequencies, and NBO charge distribution were performed by G09 at MP2/6-31g(d,p). DICE software was used by performing 500.000 MC steps. The ORDER software was also used to analyze the minimum distances between solute and solvent to describe hydrogen bonds and solvation layers.

Results

Comparing between the neutral and cationic forms of dopamine, changes in angles between bonds and rotations of the amine group concerning the aromatic ring of the catechol occurred to come closer together due to the effects of charges and stabilization of the gauche conformations. By Monte Carlo results for distal-perpendicular conformation, a

higher density of solvent molecules around the positively charged dopamine was observed. 30 water molecules describe the second solvation shell were found around neutral dopamine at 6.25 Å, while for cationic dopamine, 27 molecules of the solvent were found at 6.05 Å. The cationic form was shown to be a better donor of hydrogen bonds. Figure 2 shows the spatial configurations obtained in the simulation of molecular liquids for neutral dopamine (left) and cationic dopamine (right).

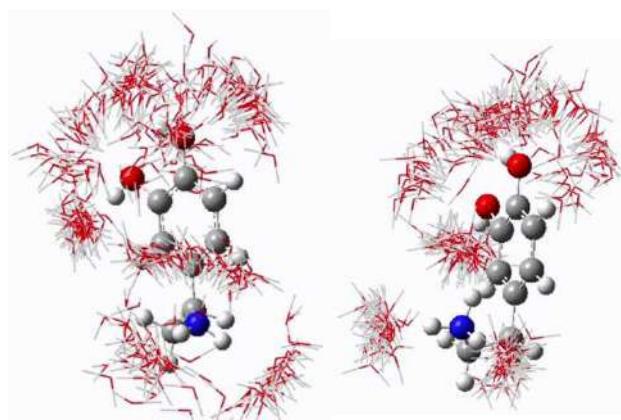


Figure 2: Snapshots obtained after dopamine solvation simulation

In the simulation of positively charged solute, the regions that solvent molecules occupy are also more restricted.

Conclusions

Cationic dopamine becomes more donor of hydrogen bonds in their polar groups. In addition, there is a higher density of water molecules around them in solution compared to neutral dopamine. We are carrying out thermodynamic calculations for the uncorrelated structures yielded by the simulation and checking other conformations out. These results will be ready for the event for a deeper analysis of the solvent effect on the solute structures.

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Electronic structure and spectroscopic properties of VAr⁺ and VKr⁺

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Palavras-Chave: Electronic structure, CASSCF/MRCI method, metal-rare-gas diatomic.

Introduction

Theoretical and experimental studies of systems containing transition metal ions and rare gases besides its intrinsic relevance in spectroscopy, also presents us challenges to understand its bonding [1]. However, these systems present inherent difficulties arising from the closeness of the energy states of the metal atom, thus leading to a relatively high density of low-lying molecular states. In this work, we described the potential energy curves (PECs) of the quintuplet states of VX⁺ (X = Ar, Kr) and determined the spectroscopic parameters associated with them.

Methods

The PECs were described using the SA-CASSCF and MRCI (including Davidson correction, +Q) methods, both with an aug-cc-pV5Z [2] basis set and implemented in Molpro [3]. For this, four electrons were distributed into a fifteen orbitals active space (7, 3, 3, 2) and vibrational and rotational constants were calculated by the program INTENSITY [4].

Results

For both systems, as shown in Fig. 1, the first and second dissociation channels are separated by 2740 cm⁻¹, in excellent agreement with the experimental excitation energy of the ion V⁺ (2720 cm⁻¹). For the third dissociation channel, it was overestimated by 1551 cm⁻¹ relative to the experimental one, even after testing various active spaces.

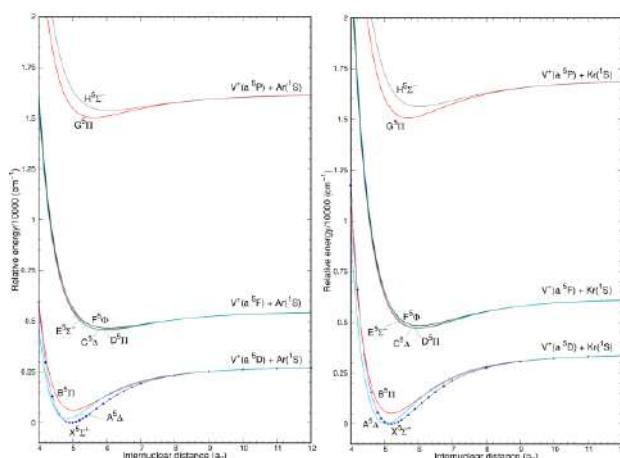


Fig. 1. PECs of the quintuplet states associated to the three lowest-lying dissociation channels of VAr⁺ (left) and VKr⁺ (right).

To make possible comparisons of spectroscopic parameters, the whole PECs associated with the third dissociation channel was rescaled by subtracting the calculated difference. For the ground state, X^{5Σ⁺, the set of parameters (R_e/a_0 , D_e/cm^{-1} , ω_e/cm^{-1}) are: VAr⁺ (4.950, 2752, 162) and VKr⁺ (5.185, 3446, 143). The dissociation energies are in good agreement with the experimental values, close to 2900 cm⁻¹ and 3800 cm⁻¹ for VAr⁺ and VKr⁺, respectively, and better than those of previous theoretical studies (2597 cm⁻¹ for VAr⁺). Similar comparisons were also done for the other electronic states. Regarding the electronic transitions, the most important one involves the states associated with the first and third dissociation channels and known experimentally as G^{5Π} - X^{5Σ⁺. We found that the radiative lifetimes of the ground vibrational states of G^{5Π} are 6.73 ns and 36.8 μs for VAr⁺ and VKr⁺, respectively. Also, the main contributions to these values are from the G^{5Π} - B^{5Π} (VAr⁺) and G^{5Π} - X^{5Σ⁺ (VKr⁺) electronic transitions. The differences between both systems may be due to the distinct shapes and shifts of the PECs relative to the other electronic states. Additionally, detailed results about the dipole moments, spectroscopic parameters, and electronic transitions are also reported.}}}

Conclusions

Nine quintet electronic states of VAr⁺ and VKr⁺ are characterized and the only transition experimentally observed so far, G^{5Π} - X^{5Σ⁺, reliably described with calculated values of transition probabilities and radiative lifetimes. It is expected that this work can guide and motivate additional experimental and theoretical investigations on diatomics of transition metal-ions and rare gases.}

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MacMillan's imidazolidinones as a solution for the asymmetric synthesis of aza-flavanones: a DFT study

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Palavras-Chave: asymmetric synthesis, heterocycles, organocatalysts

Introduction

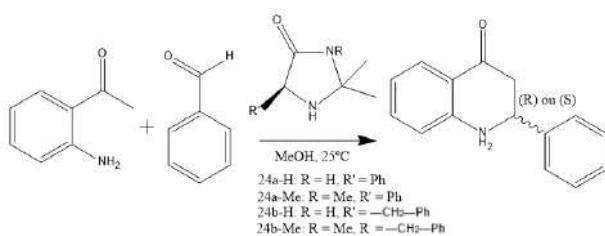
2-Aryl-2,3-dihydro-4-quinolones are aza-analogues of flavanones with potential antimalarial and anticancer applications which also serve as building blocks for a variety of compounds with pharmacological applications (1). Differences in the applications of the (*R*) and (*S*) enantiomers of the molecule have motivated the development of new, cleaner and more enantioselective strategies for obtaining either enantiomer. This present work offers theoretical insight into the viability of the synthesis of the (*S*)-2-Aryl-2,3-dihydro-4-quinolones catalyzed by MacMillan's chiral imidazolidinones, a class of organocatalysts which has yielded notable success such as in applications in the asymmetric Friedel-Crafts and Diels-Alder reactions (2).

Materials and methods

DFT (Density Functional Theory) calculations in the B3LYP/6-31G(d) levels of theory were employed for the optimization of gas phase (TS) geometries as well as thermal contributions to Gibbs Free Energy at 298.15 K. TS were characterized by computing their vibrational frequencies, which provided only one imaginary frequency. More accurate electronic energies were obtained through single point calculations in the B3LYP-D3/6-31G(d) as well as M06-2X/6-311+G(d,p) levels of theory.

Results and Discussion

In the presumed Intramolecular Mannich mechanism for the formation of 2-Aryl-2,3-dihydro-4-quinolones, the reaction between 2-aminoacetophenone with benzaldehyde yields (*E*) or (*Z*) imines. The role of the catalyst is to form an enamine intermediate, whose nucleophilic carbon would see the formation of a C—C bond with the carbon of the imine through the *Re* or *Si* prochiral faces in the “chair-like” Zimmerman-Traxler transition state of the enantioselectivity determining step of the reaction. The reaction, the selected four imidazolidinones and the simulated $\Delta\Delta G^\ddagger$ calculated as the difference between the most stable *Pro-S* with the *Pro-R* transition states are the following:



Catalyst	$\Delta\Delta G^\ddagger$ [B3LYP/6-31G(d)//M06-2X/6-311+G(d,p)] in favour of the <i>S</i> isomer
24a-H	5.9 kcal mol ⁻¹
24a-Me	5.2 kcal mol ⁻¹
24b-H	4.8 kcal mol ⁻¹
24b-Me	4.4 kcal mol ⁻¹

Analysis of the diastereoisomeric TS geometries revealed that the 24a and 24b *Pro-S* transition states presented a decisive π–H interaction only available in the cyclization through the *Si* prochiral face, while the most stable 24b *Pro-R* transition states presented repulsive arene–arene interactions. There was no evidence of plausible hydrogen bonding between the protonated imine and the N–H fragment in the 24a-H and 24b-H catalyzed reactions. The Me-substituted catalysts proved less selective than their hydrogenated counterparts due to steric repulsion between the methyl substituent and the phenyl/benzyl groups in the most stable *Pro-S* TSs. The (*Z*)-imine TSs proved to be at least at least 6 kcal mol⁻¹ more energetic than their (*E*) counterparts. Although all catalysts proved promising, yielding estimated ee% via Boltzmann factor above 99% in favor of the desired (*S*) isomer, the confirmation for the trends observed in this study must arrive through experimental means.

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Differences in the torsional anharmonicity between reactant and transition state: the case of 3-butenal + H abstraction reactions

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Palavras-Chave: torsional anharmonicity, 3-butenal, transition state.

Oxygenated compounds have attracted considerable attention in combustion chemistry due to their potential as a surrogate to conventional fuels. In an experimental study, Tian *et al.* (*Combustion and Flame*, 2011, **158**, 756–773.) investigated the furan thermal decomposition using tunable synchrotron vacuum ultraviolet (VUV) photoionization and molecular-beam mass spectrometry¹. In this work, they proposed a kinetic mechanism with 206 species and 1368 reactions, in which 3-butenal were formed in the termination steps with reactions of $\text{H}_2\text{C}=\text{CHCHCOH}$ with H-atom. In a secondary mechanism, the 3-butenal + H reactions were taken into account and the thermal rate constants estimated from the similar reactions of acetaldehyde with global rate constants given by $k(T)=4.0\times10^{12}(\text{cm}^3\text{mol}^{-1}\text{s}^{-1})\exp[-4.2(\text{kcal/mol})/\text{RT}]$.

Based on the relevance of the H-abstraction reactions of 3-butenal by hydrogen in the furan thermal decomposition and the scarce data of the overall thermal rate coefficients, this work aims to provide accurate energetic, structural, and kinetic parameters for the title reactions. The anharmonicity due to the hindered rotors of stationary point generated by the 3-Butenal + H reactions were corrected through in the rovibrational partition function, with the application of the extended two-dimensional torsional method (E2DT). To assess the accuracy of different models, we also performed the calculation of the rovibrational partition function through the multi-structural torsional anharmonicity method based on a coupled torsional potential, MS-T(C). The multipath (harmonic and anharmonic) canonical variational transition state theory (MP-CVT) with small-curvature tunneling (SCT) were calculated with Pilgrim code. All electronic structure calculations were performed at MPWB1K/6-31+G(d,p) level of theory using the GAUSSIAN 09. In the conformational search, 54 distinguishable reactant and transition states structures were found, including enantiomers, and separated into six conformational reaction channels (CRC). The individual reactive paths were constructed, variational and recrossing coefficients estimated, and the multipath rate constants obtained. No significant differences were observed between the harmonic and anharmonic partition functions of the CRC2,6 (abstraction for α -carbon of 3-butenal - R2). The barriers of interconversion between the wells of CRC2,6 are relatively greater. Thus each well

behaves close to a harmonic oscillator but with lower torsional frequencies than normal-mode frequencies associated with the torsions. Therefore, the ratio between the anharmonic (E2DT or MS-T(C)) and harmonic (MS-HO) partition function produces an anharmonic greater than unity. The differences in the anharmonic factor for 3-butenal and CRC2,6 lead to large multiplicative coefficient values to account for the torsional anharmonicity for R2. Finally, the anharmonic MP-CVT/SCT thermal rate constants of each CRC and overall process, including torsional anharmonicity with E2DT and MS-T(C), were fitted to the following equation

$$k(T) = A \left(\frac{T}{300} \right)^n \exp \left[\frac{-E(T+T_0)}{T^2+T_0^2} \right]$$

where A, n, T_0 , and E are the fitting parameters.

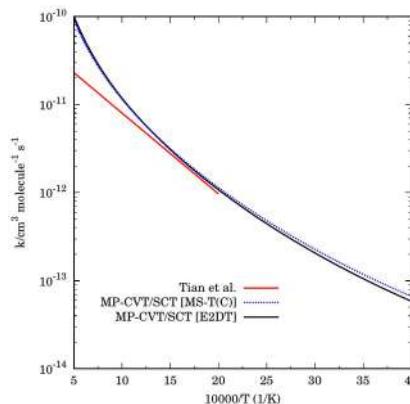


Figure 1. Arrhenius plot showing the MP-CVT/SCT total rate constants with anharmonic corrections estimated with E2DT and MS-T(C) methods. Previous estimation by Tian *et al.* are also shown.

The total thermal rate constants do not present a linear behavior. Consequently, the activation energy computed from the slope of the Arrhenius plot depends on the temperature. We obtain a variation of the activation energy between 1.86 and 14.58 kcal/mol (200 – 2500 K). In this case, the use of the conventional Arrhenius equation in these circumstances is inadequate.

Acknowledgments

The authors are grateful to CNPq and CAPES.



POLARIZABILIDADES ATÔMICAS E DE GRUPOS FUNCIONAIS DA SÉRIE DE BIOMOLÉCULAS L-GLY PARA APLICAÇÃO ELETRO-ÓPTICAS

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Palavras-Chave: Biomoléculas, Polarizabilidades, eletro-ópticas.

INTRODUÇÃO E OBJETIVOS

Para determinar propriedades de materiais moleculares com aplicações ópticas lineares desejáveis, como birrefringência e índice de refração são necessários cálculos em fase sólida, mas o custo computacional impede simular as propriedades com alta precisão. Assim, este trabalho objetiva construir progressivamente agregados de biomoléculas, e então extrair as propriedades desses blocos como se fossem do cristal, por meio de particionamento. Com auxílio da teoria quântica de átomos em moléculas (TQAIM), pode-se extrair átomos e grupos e estimar suas melhores polarizabilidades. E com esses dados propor métodos alternativos para determinar as propriedades, baseando-se em unidades poliméricas e grupos funcionais.

MÉTODOS E RESULTADOS

As posições atômicas das macromoléculas da série de L-glicina foram retiradas do Cambridge Structural Database (CSD código: 853911 (L-GLY), 1169395 (L-DIGLY), 1270317 (L-TRIGLY), 993137 (L-TETRAGLY) e 993138 (L-PENTAGLY), respectivamente) e mantidos fixados em todos os cálculos. As ligações dos átomos de hidrogênio nas estruturas foram definidas para reproduzir a média X – H de distâncias calculadas a partir de experimentos de difração de nêutrons. Os cálculos de estrutura eletrônica das moléculas isoladas foram em B3LYP usando o programa Gaussian 16¹. As densidades de carga molecular foram particionadas usando QTAIM com o software AIMAll². E para calcular os tensores de polarizabilidade atômicas e de grupo funcional foi usado PolaBer³. As componentes do tensor de polarizabilidade para as regiões atômicas podem ser obtidas através da derivada numérica do dipolo momento (1) em relação ao campo aplicado.

$$a_{ij}(\Omega) = \lim_{F_j^{\text{ext}} \rightarrow 0} \frac{\mu_i^{F_j^{\text{ext}}}(\Omega) - \mu_i^0(\Omega)}{F_j^{\text{ext}}} \quad (1)$$

Tendo como referência o grupo amina das biomoléculas e indo adicionando um bloco L-GLY para chegar a L-PENTAGLY, observa-se um acréscimo significativo na polarizabilidade isotrópica (α_{33}) e anisotrópica ($\Delta\alpha$). Analisando os grupamentos atômicos de nitrogênio terminais de cada molécula observa-se um aumento de 10,076% na polarizabilidade N(5) da (L-DIGLY) em relação a N(3) da (L-GLY) e o aumento foi maior quando se compara N(3) com N(7) da (L-TRIGLY) de 11,824%. Quando se analisa N (3) com N (9) e N(11) das biomoléculas com quatro e cinco blocos de L-GLY, observa-se uma pequena adição de 1,337% em relação a N(9) e em N(11) de 6,692%. Essa variação na polarizabilidade na L-TETRAGLY e L-PENTAGLY pode estar relacionada com adição de blocos L-GLY fora do plano de polarização da molécula. A análise aponta que o efeito da polarização atômica influencia as ligações de hidrogênio com

aumento significativo no volume dos átomos de oxigênios e especialmente nos átomos de nitrogênios.

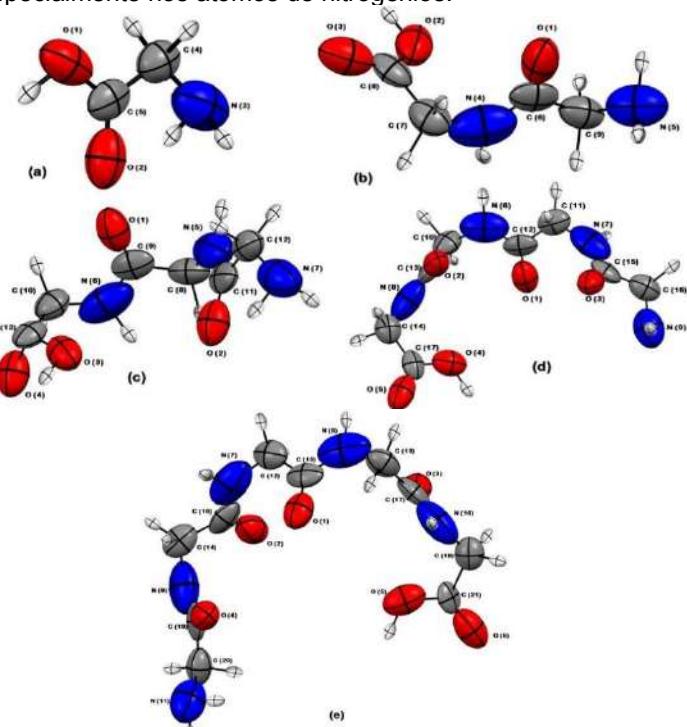


Figura 01: Polarizabilidades das macromoléculas (a) L-GLY, (b) L-DIGLY, (c) L-TRIGLY, (d) L-TETRAGLY e (e) L-PENTAGLY

CONCLUSÕES

Ao se analisar os grupos atômicos e funcionais, observa-se que o nitrogênio dos grupamentos amino ($-\text{NH}$ e $-\text{NH}_2$) e oxigênios dos grupos carboxílicos ($-\text{COOH}$), apresentam uma maximização das polarizabilidades das biomoléculas da série da L-glicina, ao mesmo tempo que eles aumentam sua anisotropia, na qual se pode relacionar com as ligações de hidrogênio que ocorrem com esses grupos. Uma observação importante em relação ao volume é quando moléculas são adicionadas fora do plano as polarizabilidades isotrópicas e anisotrópicas diminuem. A polarizabilidade isotrópica e sua anisotropia para os blocos construtores dos grupos funcionais determinam as informações das propriedades eletro-ópticas em sistema gasoso, os resultados apresentados podem ajudar a produzir em laboratórios materiais eficientes.

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Influência do Efeito Solvente na Atividade Óptica do R-OP e S-Naproxeno.

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Palavras-Chave: rotação específica, dicroísmo circular, efeito solvente.

Introdução

O procedimento de cálculo da atividade óptica é bem descrito na literatura, com diversos protocolos¹. Entretanto, para alguns solventes a atividade óptica é difícil de se prever, como visto atualmente no trabalho de Ximenes e colaboradores². Nesse contexto, esse trabalho tem o objetivo de investigar o efeito solvente na atividade óptica do R-Óxido de Propileno (R-OP) e S-Naproxeno.

Metodologia

Fez-se análise de ORD para R-Óxido de Propileno e ECD para S-Naproxeno. Inicialmente, incluiu o solvente por metodologias contínuas de solvatação (SMD, IEFPCM). Posteriormente, adicionou o solvente explícito com Monte Carlo (software DICE³), utilizou-se a primeira e segunda camada de solvatação para calcular o ORD e ECD. Por fim, adicionou-se explicitamente o solvente pelo modelo de solvatação cúbica⁴, para isso a posição do solvente foram optimizadas com UFF e, logo depois, por mecânica Quântica. Os cálculos com modelos implícitos foram realizados com o software gaussian16 combinando os funcionais B3LYP, CAM-B3LYP, M06-2X, ω B97XD com as funções de base 6-311++G(2d,p), 6-311++G(3df,2p), aug-cc-pVDZ, aug-cc-pVTZ, Def2-SVP, Def2-TZV sem e com a adição de dispersão empírica (B3LYP/GD3BJ, CAM-B3LYP/GD3BJ, M06-2X /GD3 e ω B97XD /GD2). Calculou-se o espectro de ORD nos comprimentos de onda de 300,00nm – 400,00nm – 500,00nm – 589,30nm – 600,00nm e 700,00nm e ECD com 40 níveis de excitação (TD-DFT). A simulação com o software DICE fez-se em uma Caixa cúbica, NTP ensemble, 1000 moléculas com $5 \cdot 10^5$ passos de Monte Carlo (MC) para termalização e $1 \cdot 10^5$ passos de MC para etapa de equilíbrio. Logo após, o ECD e ORD foram calculados em M062X-6-31G(d). Para os cálculos com modelo de Caixa cúbica utilizou-se UFF como pré-optimização do Sistema, seguido pelo nível M062X/6-31G(d) para otimização e atividade óptica (ORD, ECD).

Resultados e Discussão

A rotação específica para R-OP em Benzeno, Metanol e água, estão apresentados na Tabela 1. Os valores para solvente implícito falam na descrição do metanol. Com utilização do solvente vindo da simulação com DICE, os valores da primeira camada de solvatação assumem os sinais corretos e se

aproximam do experimental ao englobar a segunda camada de solvatação. A descrição com a caixa cúbica não apresenta os mesmos sinais que o experimental⁵ (assim como na solvatação implícita).

Tabela 1 - Valores de ORD em 589 nm para R-OP.

Solvente	SMD	DICE 2 CS	CB	Exp. ⁵
Água	-1,01	-3,06	37,68	-4,3
Benzeno	18,60	22,23	30,27	30,6
Metanol	-0,44	7,02	-15,55	7,2

Ao avaliar o ECD com metodologia implícita, tem-se resultados semelhantes ao da literatura² e também não conferem com os sinais experimentais. Os resultados de solvatação explícita com DICE e caixa cúbica apresentam os mesmos perfis para o espectro (Figura 1). Ambas metodologias acertam o sinal em acetonitrila, porém possuem a descrição invertida em relação ao etanol.

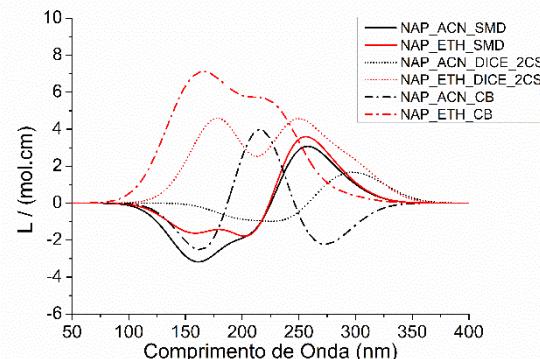


Figura 1 - Espectro de ECD das configurações de S-Naproxeno em acetonitrila (ACN) e etanol (ETH).

Especula-se que o solvente explícito e as abordagens com espectros envolvendo configuração (ponderadas por Boltzmann) não são suficientes, com a função de base como potencial para ajustar melhor o espectro ao experimental, sendo as próximas etapas o desenvolvimento de base para descrição de ECD.

Agradecimentos

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Position Sampling and Analysis of the Interaction Between TiO_2 and Deprotonated NKX-2553 Dye

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Key Words: Photosensitive Dyes, Monte Carlo Simulations, TiO_2 anatase nanoparticle.

Titanium dioxide has great technological importance and is used in most photocatalytic processes and in photoelectrochemistry [1]. Most photovoltaic cells are based on thin granular titanium oxide films [2] [3] [4] and several studies have been carried out in this area, with the aim of improving the photocatalytic efficiency [5] and also studying the synthesis of different forms of TiO_2 nanomaterials [6]. In the literature it is found that the most stable form found is TiO_2 anatase (101). In this work, we study the interaction of the photosensitive organic dye and the nanoparticle. Starting from an initial configuration composed by the deprotonated NKX-2553 [7] dye and an amorphous TiO_2 nanoparticle [8], one hundred classical Monte Carlo simulations were performed with the objective of sampling preferential regions of interaction and an anchorage position of the dye in the nanoparticle. The TiO_2 nanoparticle used in the simulations is composed of 14 titanium and 28 oxygen. Analyzing the nanoparticle + dye configurations coming from the simulations, in a total of around 45,800 configurations, we looked for interactions of the type $\text{Ti} \rightarrow \text{O}$, $\text{Ti} \rightarrow \text{N}$ and $\text{O} \rightarrow \text{H}$. Usually the anchoring process occurs through acid groups such as $-\text{COOH}$ and, in our case, we obtained a higher percentage of $\text{Ti} \rightarrow \text{O}$ interaction, as already predicted. Summarizing, of the total configurations analyzed, we found around 58% of the $\text{Ti} \rightarrow \text{O}$ interactions, 22% of the $\text{O} \rightarrow \text{H}$ type and 8% of the $\text{Ti} \rightarrow \text{N}$ type. We can also think about which configuration has the greatest interaction energy. After analyzing the simulations, we realized that the $\text{O} \rightarrow \text{H}$ interaction has an interaction energy of -61.63 kcal/mol, being the highest energy when compared to the others. So, eventually it is possible to have two or more specific interactions and in this case interactions of the type $\text{O} \rightarrow \text{H}$ and $\text{Ti} \rightarrow \text{O}$. Once the anchoring position was determined, now simulations involving the dye, TiO_2 nanoparticle and acetonitrile solvent are being carried out. Our main questions are: (i) Does the nanoparticle structure (amorphous, crystalline or a larger structure) interfere in the absorption spectrum of the photosensitive dye? (ii) Is the spectrum affected by the TiO_2 structure and the specific anchorage location of the dye? (iii) How should the oxidized dye restoration process occur, in this situation in which we treat the nanoparticle system, deprotonated dye anchored to the nanoparticle, solvent medium and iodide?

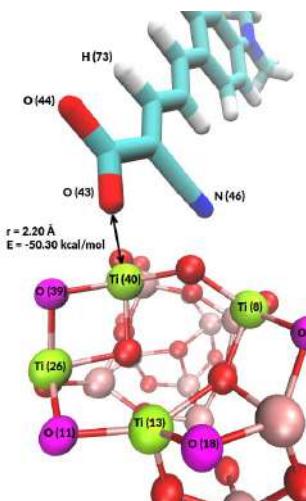


Figure 1: Schematic representation of the atoms that most contribute to the interaction and anchorage of the dye to the nanoparticle. The main titanium and oxygens are represented in highlighted yellow and magenta colors. Ti(40) presented an average distance around 2.20 Å to the O(43) and O(44) oxygens of the dye, with an average energy of interaction of pairs of -50.30 kcal/mol.

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Aspectos Qualitativos do solvatocromismo das espécies I_2 , I^- e I_3^- : Análise teórico-experimental

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Palavras-Chave: *Iodo, Iodeto, Triiodeto.*

INTRODUCÃO

Sabe-se que a coloração da solução de iodo (I_2) depende da natureza do solvente.¹ Silva e colaboradores² realizaram um estudo com o objetivo de obter um melhor entendimento do efeito solvatocrômico do I_2 , mas inicialmente a concordância dos resultados teóricos e experimentais foram pouco satisfatórios. Maia e colaboradores³ indicaram a possibilidade de formação de íons triiodeto (I_3^-) a partir do iodo (I_2) e íons iodeto (I^-) em solução, assim surgiu a necessidade de investigar se essas espécies aniônicas também apresentavam solvatocromismo. Assim, este trabalho tem por objetivo investigar por meio da espectrofotometria UV-VIS e cálculos TD-DFT, o efeito do solvente sobre as espécies I^- e I_3^- comparando aos análogos obtidos para o I_2 .

METODOLOGIA

Procedimento Experimental: Para preparo das soluções de iodo metálico (I_2), iodeto de potássio (KI), triiodeto (I_3^- , mistura KI+ I_2) e obtenção dos espectros experimentais foram utilizados 5 solventes P.A.: clorofórmio, acetato de etila, etanol 95%, metanol e água destilada. As concentrações padrão para as soluções foram: I_2 25 mg L⁻¹, KI e I_3^- 6,66 mg L⁻¹, exceção clorofórmio 1000 mg L⁻¹.

Detalhes Computacionais: As geometrias de equilíbrio foram obtidas, inicialmente em fase gasosa no nível B3LYP/6-311G(d,p). Os espectros teóricos, aqui apresentados, foram obtidos via TD-DFT com os funcionais CAM-B3LYP, B3LYP e ω B97XD mantendo o conjunto de base 6-311G(d,p) para I_2 , I^- e I_3^- , respectivamente. Também foi incluído o modelo PCM e duas moléculas explícitas de cada solvente. Os cálculos foram executados no Gaussian 09W.⁴

RESULTADOS & DISCUSSÃO

A Figura 1 mostra o efeito do solvente sobre as espécies I_2 , I^- e I_3^- . Para I_2 nota-se uma coloração violeta para solventes de menor polaridade, passando por coloração alaranjada para solventes de polaridade intermediária e coloração que varia de amarelo ao castanho claro para solventes de maior polaridade.

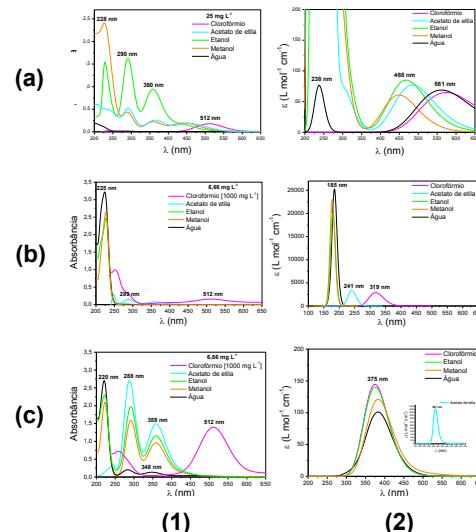
Figura 1 – Solvatocromismo das espécies (a) I_2 , (b) I^- e (c) I_3^- , nos solventes clorofórmio (1), acetato de etila (2), etanol (3), metanol (4) e água (5).



Para o ânion I^- , nota-se que as soluções são praticamente incolores. E para o íon I_3^- a coloração das soluções é amarela, com exceção do clorofórmio que apresentou coloração violeta.

A Figura 2 mostra os espectros experimentais obtidos através da espectrofotometria no UV-VIS e calculados via TD-DFT para as espécies a) I_2 , b) I^- e c) I_3^- em diferentes solventes.

Figura 2 – Espectros experimentais (1) e calculados (2) das espécies a) I_2 , b) I^- e c) I_3^- em diferentes solventes.



CONSIDERAÇÕES FINAIS

A coloração das soluções de I_2 e I_3^- variam de violeta ao amarelo. Embora as soluções do ânion I^- sejam praticamente incolores, exceção clorofórmio, observa-se uma boa correlação do aspecto visual com os espectros teórico-experimentais obtidos. Vale destacar a repetição do máximo de absorção em 512 nm (solução de clorofórmio) nos espectros experimentais das três espécies estudadas.

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Análise teórico-experimental dos comprimentos de onda de máxima absorção das espécies I_2 , I^- e I_3^- em diferentes solventes

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Palavras-Chave: *iodo, iodeto, triiodeto.*

INTRODUÇÃO

Sabe-se que o iodo apresenta solvatocromismo¹. Maia e colaboradores² observaram que, assim como essa molécula, suas espécies iônicas apresentam características semelhantes.

Este trabalho realizou uma investigação teórico-experimental dos comprimentos de onda de máxima absorção das espécies iodo (I_2), iodeto (I^-) e triiodeto (I_3^-), em diferentes solventes, através de cálculos químicos-quântico via TD-DFT (Time Dependent - Density Functional Theory) e espectrofotometria UV-VIS.

METODOLOGIA

Detalhes computacionais

As otimizações das geometrias foram obtidas, inicialmente, em fase de gás no nível B3LYP/6-311G(d,p). Para obtenção dos máximos de absorção ($\lambda_{\text{máx.}}$) foram realizados cálculos TD-DFT com diferentes funcionais: B3LYP, PBE1PBE, CAM-B3LYP, M06-2X e ω B97XD e conjunto de base 6-311G(d,p). Para todos os cálculos, empregou-se o modelo implícito de solvatação PCM (*Polarizable Continuum Model*) e moléculas explícitas a fim de obter uma melhor representação das condições experimentais. Todos os cálculos foram executados no software Gaussian 09W.³

Procedimento experimental

Para preparo das soluções de iodo metálico (I_2 , marca NEON), iodeto de potássio (KI, marca Dinâmica) e triiodeto (I_3^- , mistura KI+ I_2) foram utilizados 5 solventes P.A.: clorofórmio (Confiança CRQ), acetato de etila (Vetec química fina), etanol 95% (Cromoline química fina), metanol (Exodo científica) e água destilada. As concentrações das soluções para obtenção dos máximos de absorção ($\lambda_{\text{máx.}}$) foram: 25 mg L⁻¹ para o I_2 e 6,66 mg L⁻¹ para KI e I_3^- , com exceção do clorofórmio 1000 mg L⁻¹.

RESULTADOS & DISCUSSÃO

A Tabela 1 apresenta os desvios absolutos médios (dam) dos máximos de absorção ($\lambda_{\text{máx.}}$) calculados em relação aos análogos experimentais para as espécies I_2 , I^- e I_3^- , em 5 diferentes solventes e funcionais, com diferentes abordagens teóricas.

Tabela 1 – dam dos $\lambda_{\text{máx.}}$ (nm) calculados em relação aos análogos experimentais para as espécies I_2 , I^- e I_3^- com diferentes abordagens teóricas.

	B3LYP	PBE1PBE	CAM-B3LYP	M06-2X	WB97XD	dam
$I + 1$ molécula explícita de solvente (fase de gás)						
dam	22	37	39	40	45	37
$I + 1$ molécula explícita de solvente + PCM						
dam	55	48	58	55	61	55
$I + 2$ moléculas explícitas de solvente (fase de gás)						
dam	35	41	36	34	42	38
$I + 2$ moléculas explícitas de solvente + PCM						
dam	41	43	51	46	57	48
Molécula isolada I_2						
dam	89	92	89	81	87	88
$I_2 + 1$ molécula explícita de solvente (fase de gás)						
dam	186	177	167	213	168	182
$I_2 + 1$ molécula explícita de solvente + PCM						
dam	160	153	146	205	146	162
$I_2 + 2$ moléculas explícitas de solvente (fase de gás)						
dam	113	108	98	141	99	112
$I_2 + 2$ moléculas explícitas de solvente + PCM						
dam	104	106	88	128	91	103
Molécula isolada I^-						
dam	82	74	52	60	54	64
$I^- + 1$ molécula explícita de solvente (fase de gás)						
dam	89	80	58	70	52	70
$I^- + 1$ molécula explícita de solvente + PCM						
dam	69	65	50	59	47	58
$I^- + 2$ moléculas explícitas de solvente (fase de gás)						
dam	86	77	51	58	46	64
$I^- + 2$ moléculas explícitas de solvente + PCM						
dam	54	57	46	55	42	51

Os menores desvios foram obtidos para o íon I^- , com 1 molécula explícita de solvente em fase gasosa. Os melhores resultados para a espécie I_3^- foram conseguidos quando se utilizou duas moléculas explícitas de solvente e modelo PCM. Todas as abordagens utilizadas apresentaram elevados desvios para o I_2 , o que sugere uma maior concentração das formas aniônicas em solução.

CONSIDERAÇÕES FINAIS

Uma melhor concordância observada entre os resultados, teóricos e experimentais, para o íon I^- podem sugerir uma elevada concentração dessa espécie nas diferentes soluções estudadas. Os funcionais B3LYP e ω B97XD apresentam um melhor desempenho, frente aos resultados experimentais, para os íons iodeto e triiodeto, respectivamente. Para o I_2 os menores desvios foram conseguidos utilizando a molécula de soluto isolada.

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Pt adsorption in Borophene nanosheet for sensor gas: a density functional theory

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Palavras-Chave: Borophene, Density Functional Theory, Pt adsorption.

Borophene is a single layer of boron atoms, which has recently been synthesized on Ag substrates¹. All the four phases (2-P_{mmn} , β_{12} , χ^3 and honeycomb phase) of borophene are metallic². Due to the unique physical and chemical properties, borophene presents potential applications, such as, sensor, hydrogen storage, Li-S batteries, supercapacitor, etc. Borophene also exhibits catalytic properties in hydrogen evolution, oxygen reduction, oxygen evolution as well in CO_2 electroreduction reaction. In this study, using density functional theory (DFT) calculations we investigate the structural, energetic and electronic properties of Pt adsorption in β_{12} phase of borophene nanosheet. The aim of this work is to investigate the Pt decorated borophene for the gas sensor of two important molecules: carbon monoxide (CO) and nitrogen monoxide (NO). These molecules are common air pollutants and dangerous for the environment. DFT calculations are performed with the Vienna ab initio simulation package (VASP) within generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (PBE) to modulate the exchange-correlation functional. The basis set is constructed using plane waves with a kinetic energy cutoff of 500 eV. To calculate the periodic functions, the sample of k-points in the Brillouin zone (BZ) are generated using the Monkhorst-Pack (MP) scheme through a 8x6x1 grid. To obtain the energetic stability (equilibrium geometry) of the pristine and functionalized structures the conjugated gradient (CG) method is used and the forces on the atoms are calculated using the Hellmann-Feynman procedure. In our calculation no constraints are imposed, all atoms in the supercell are allowed to relax until the forces are smaller than -0.025 eV/Å, without imposing any symmetry. The DFT-D2 method of Grimme is used to capture the dispersive forces and describe the interactions between Pt doped atom and adsorbed molecules. For Pt adsorption we investigated seven configurations: (a) in top of B hexacoordinate, (b) in top of B pentacoordinate, (c) in top of B tetracoordinate, (d) between the B-pentacoordinate and B-pentacoordinate bonds, (e) between the B-tetracoordinate and B-hexacoordinate bonds, (f) between the B-tetracoordinate and B-tetracoordinate bonds and, (g) in center of hexagon. We observed that the most stable configuration (lower binding

energy) for the Pt atom is in the center of the hexagon (-4.523 eV). The CO and NO molecules are preferentially adsorbed (lowes energy) with the molecular axis perpendicular to the Pt atom. The adsorption energies are -1.977 and -2.495 eV, for the CO and NO molecule, respectively. This binding energy indicates a strong interaction between the Pt-doped borophene and the molecules. The C-O and N-O bond distances are increased by 4% and 3% as compared to the isolated molecules, in agreement with the adsorption energies. Our results present that the Pt-doped borophene is a potential material to be used as a gas sensor.

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Interpretação da Cinética Super-Arrhenius em Processos Biológicos: Incorporação da Relação de Kramers-Stokes-Einstein

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Palavras-Chave: Super-Arrhenius, transitividade, constante cinética.

Dentre os comportamentos não-lineares no diagrama de Arrhenius, $\ln k$ vs $1/T$, o super-Arrhenius (convexo) – onde os fenômenos de transporte aceleram os processos à medida que a temperatura aumenta – é encontrado em um conjunto amplo de fenômenos, especialmente em processos biológicos [1,2].

Aqui incorporamos alguns modelos previstos na literatura que podem descrever esses desvios: i) Teoria de Kramers, correlaciona constantes cinéticas de reação com o inverso da viscosidade η do solvente, sendo a viscosidade representada pela formulação de Stokes-Einstein, ii) o modelo de Aquilanti-Mundim [3], inspirado na termodinâmica não-extensiva de Tsallis, capaz de descrever esses desvios a partir do parâmetro d e iii) mais recentemente, nosso grupo propôs o diagrama baseado na função Transitividade [4]. A Transitividade é definida em termos do inverso da derivada logarítmica da constante cinética k em função de β , interpretada como tempo de visitação dos estados energéticos envolvidos no processo dinâmico. A proposição do formalismo de Aquilanti-Mundim e a relação de Kramers-Stokes-Einstein, nos permite comprovar as condições em que existe descontinuidade real nos sistemas estudados. A equação para a Transitividade obtida a partir do nosso modelo é expressa como:

$$\gamma(\beta) = \frac{1}{E_a} \left(1 - \frac{\mu_0 (1 - d\epsilon_v \beta)^{\frac{1}{d}-1} \epsilon_v}{E_a \sqrt{\mu_0^2 (1 - d\epsilon_v \beta)^{\frac{2}{d}} + 4\omega^2}} \right)^{-1} \quad (1)$$

onde μ_0 é a fricção, definida por $\mu = 6\pi\eta R/M$, ϵ_v e E_a são parâmetros energéticos da barreira de ativação, onde ϵ_v pode estar conectado com parâmetros termodinâmicos, ω é a frequência imaginária do estado de transição e $d \equiv RT^\dagger/\epsilon_v$ é o parâmetro de deformação, onde para os casos super-Arrhenius, $\epsilon_v^\dagger = RT^\dagger$ marca a mínima energia para o sistema ser "ativo".

O modelo da Transitividade, quando tende a valores limites, converge para modelos convencionais: A lei de Arrhenius é recuperada nos limites em que (i) $\beta \rightarrow 0$ e (ii) $\beta \rightarrow 1/d\epsilon_v$, resultando nas equações $\gamma(\beta) = 1/E_a$ e $\gamma(\beta) = 1/(E_a - \epsilon_v/2\omega)$ respectivamente. Se (iv) $\mu_0^2 (1 - d\epsilon_v \beta)^{\frac{2}{d}} \gg 4\omega^2$ – configurando alta fricção – pode-se inferir, na equação resultante, que se $\beta \rightarrow 0$ e $\beta \rightarrow \infty$, a lei de

Arrhenius também é recuperada na forma $\gamma(\beta) = 1/(E_a - \epsilon_v)$ e $\gamma(\beta) = 1/E_a$ respectivamente.

As formulações baseadas no conceito de Transitividade foram aplicadas à descrição de diversos fenômenos sobre a dependência da temperatura de processos de constantes cinéticas além de Arrhenius e Eyring [5]. Na Figura 1 está representado o diagrama da Transitividade, γ vs $1/T$, de um resultado parcial para o batimento cardíaco de tartarugas [6] onde os dados foram ajustados utilizando nosso modelo da Transitividade. Os parâmetros E_a e ϵ_v são expressos em $\text{kJ}\cdot\text{mol}^{-1}$, ω e μ_0 em s^{-1} , e o parâmetro d é adimensional.

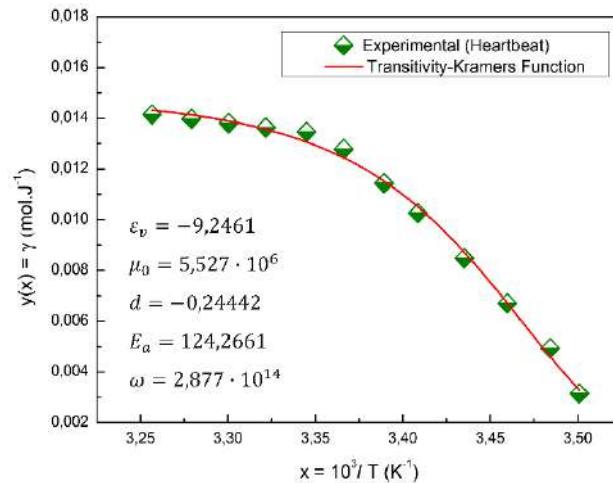


Figura 1. Diagrama da Transitividade do processo biológico “batimento cardíaco da tartaruga”. Losangos: dados do recíproco da energia de ativação do sistema obtidos numericamente; Curva: modelo da Transitividade.

Observa-se que os dados experimentais exprimem um comportamento super-Arrhenius, onde a adequação do modelo da Transitividade aos dados da dependência da temperatura do processo pode ser um indicativo de que o sistema pode ser descrito por uma função contínua e sem a necessidade de definir o conceito de “Arrhenius-Break Temperature”.

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Theoretical predictions of the dipole moments of deuterated pyrene ($C_{16}H_{10}$) and peropyrene ($C_{26}H_{14}$) isotopologues

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Keywords: accurate dipole moments, deuterated systems, isotopologues, beyond Born-Oppenheimer.

Synopsis We applied an adiabatic beyond Born-Oppenheimer electronic plus a zero-point vibrational correction methodologies implemented in the Dalton code[1] to calculate for the first time isotopic dipole moments of deuterated pyrene ($C_{16}H_{10}$) and peropyrene ($C_{26}H_{14}$), isotopologues. This approach was used previously to predict the isotopic effect on dipole moments in a variety of apolar and polar molecules[5, 6, 7].

Small dipole moments which appear in apolar molecules subject to isotopic substitution (mainly deuteration) offer potential for high resolution spectroscopy, since these molecules possess pure rotational spectra. The dominant effect on the dipole moments comes from the changes of the molecular vibrational modes due to the larger inertia of the heavier isotopes.

A smaller but still measurable contribution comes from the electronic symmetry breaking due to the different isotopic mass and thus cannot be analyzed theoretically under the usual clamped-nuclei Born-Oppenheimer (BO) approximation.

To compute the breaking symmetry effect we employed an adiabatic correction called Finite Nuclear Mass Correction (FNMC)[2]. In order to account the vibrational effect we used the zero point vibrational correction (ZPVC) method, which consider the anharmonic force field and deviation from linearity of the molecular property[3].

Here, DFT-B3LYP-6-31G** finite nuclear mass correction (FNMC) calculations of vibrationally averaged (ZPVC) isotopic dipole moments of deuterated isotopologues of pyrene ($C_{16}H_{10}$) and peropyrene ($C_{26}H_{14}$), are reported[4].

Those molecule was chosen because of their importance in many basic and applied fields, particularly in astrochemistry and atmospheric chemical-physics.

The choice of the deuteration positions was made in order to obtain the maximum isotopic asymmetry and we observed the same tendency of competition between the electronic and vibrational contributions that we perceive for several systems[5, 6, 7]. We also observed an increase of the dipole moment components values with deuteration similar to the one obtained in the case of the deuterated benzenes[5].

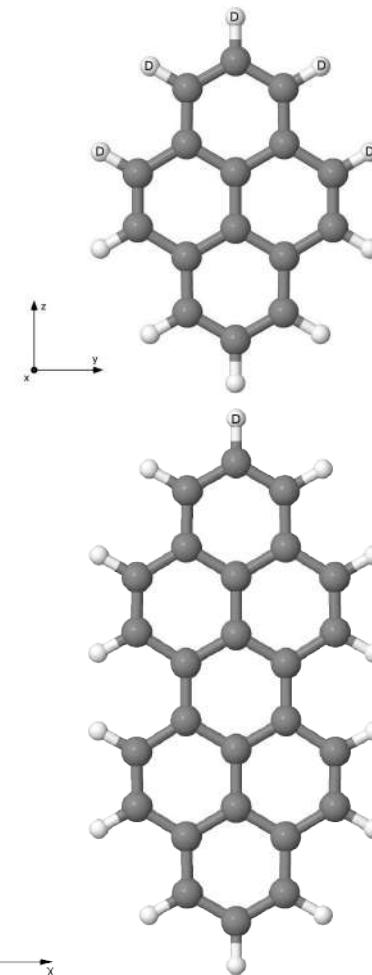


Figure 1. Illustration of the isotopic asymmetry configuration of two variants of deuterated pyrene and peropyrene isotopologue.

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S_N1 vs S_N2 on sp³ carbon: exploring structural and electronic effects of substrate by DFT

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Keywords: Nucleophilic Substitution, Borderline Mechanisms, DFT

INTRODUCTION

Nucleophilic aliphatic substitution reactions constitute important steps in the synthesis of substances with biological activity and industrial appeal. Unimolecular (S_N1) and bimolecular (S_N2) pathways can be thought as limiting cases of a mechanistic continuum. In between them, borderline mechanisms are proposed. The preference for one path over another depends on several factors, such as the structure of the substrate, the nucleophile and the solvent used.^{1,2} This plurality is still a topic of discussion and needs further analysis. In this context, the present work aims to rationalize the preferential reaction pathway for nucleophilic aliphatic substitutions, whose substrates do not fit exclusively in the uni- and bimolecular models, by identifying lower energy reaction pathways due to structural and electronic characteristics.

METHODOLOGY

The calculations were performed using Density Functional Theory (DFT), with the computational method M06-2X/aug-cc-pVTZ, previously validated according to geometrical and energetic parameters. To determine the reaction pathway (S_N1 or S_N2), we evaluated substrates whose electrophilic carbons do not fit exclusively in the limiting mechanistic models, that is, secondary (A), hindered secondary (B) and α -heteroatom (C) – Figure 1. The chloride anion was simulated as a nucleophile in all cases. Moreover, the effect of a solvent with high dielectric constant (formamide) was verified for substrate 1A.

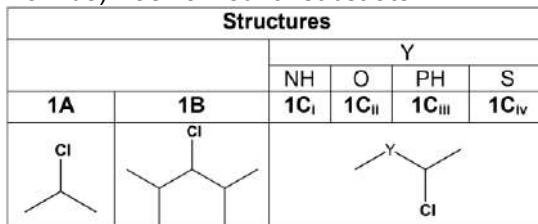


Figure 1: Structures of evaluated substrates in the mechanisms of uni- and bimolecular nucleophilic substitution.

RESULTS

Table 1 shows the activation energy values for S_N2 (E_{AT}) and for carbocation formation for S_N1 (E_{C+}). The preference for a reaction pathway arises from kinetic factors. As the barrier for the formation of the carbocation is low, being often not found, E_{C+} was chosen as an evaluation parameter for the unimolecular pathway.

Table 1: E_{AT} and E_{C+} values (kcal mol⁻¹), obtained with M06-2X/aug-cc-pVTZ.

Substrates	E_{AT} (Kcal.mol ⁻¹)	E_{C+} (Kcal.mol ⁻¹)
	S _N 2	S _N 1
1A	20.83	187.74
	25.31 *	48.16 *
1B	21.14	175.72
1C _i	a	136.18
1C _{ii}	10.80	163.61
1C _{iii}	20.26	164.63
1C _{iv}	18.89	161.41

*implicit solvation “SCRF= (IEFPCM, solvent= formamide)”.
a = optimization yielded the carbocation.

The bimolecular mechanism proved to be preferable for most substrates, presenting lower barriers in the gas phase, except for the 1C_i, in which the optimization of the transition state relative to S_N2 pathway yielded the carbocation. Furthermore, the vicinal oxygen atom stabilizes the S_N2 transition state (TS) more (ca. 10 kcal mol⁻¹ relative to the secondary substrate, 1A) in comparison to other α -heteroatoms despite of its higher electronegativity. The results obtained considering implicit solvation for substrate 1A show the influence of the solvent on the ion stabilization, which is more expressive in the unimolecular path, with a considerable decrease in the energy of carbocation formation (from 187.7 kcal mol⁻¹ to 48.2 kcal mol⁻¹). Looking forward, we will simulate other substrates (e.g., allylic and benzylic) in gas and solvated phases. We intended to rationalize the electronic and structural factors that favor one mechanism over the other, according to the distortion/interaction model and to the energy decomposition analysis.

CONCLUSIONS

The simulations reveal that S_N2 pathway is favored over S_N1 for the assessed substrates, except for 1-chloro-N-methylethanamine. The vicinal oxygen atom exhibited a remarkable stabilization of the S_N2 TS. In addition, the effect of the solvent in this type of reaction was evident, especially stabilizing the ions present in the reaction steps.

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DFT studies on the mechanism of the Wang reaction for formation of 4-phenylquinazoline

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Keywords: Reaction Mechanisms, Density Functional Theory, Carbodiimide.

Introduction

An interesting reaction was discovered by Wang *et. al.* when mixing thiourea and 2-aminobenzophenone in DMSO (dimethyl sulfoxide) at 150°C. According to these authors, thiourea decomposes to form H₂S and carbodiimide (HN=C=NH), of which, the latter proceeds to react with 2-aminobenzophenone in several consecutive elementary steps to form 4-phenylquinazoline.^{1–3}

The present work focuses on the mechanism proposed by them for the reaction between carbodiimide and 2-aminobenzophenone.

Methodology

All intermediates and transition states involved in the mechanism proposed by Wang *et. al.* were optimized, with the exception of those involved in the reduction step.

All calculations were done using the Gaussian09 package and the DFT method with the density functional/basis set pair: M06-2X/6-31+G(d,p). In some cases, Spartan16 package was employed for conformational searches before optimization, using molecular mechanics (force field MMFF) and/or the AM1 semi-empirical method.

The calculations were performed without solvent and the thermodynamic data was obtained from frequency calculations at 423.15K (150°C).

All transition states' imaginary frequencies were verified, and their connectivity was confirmed by IRC calculations.

Results

The structures of the intermediates are shown along the Gibbs energy curve obtained for the reaction in **Scheme 1**. Having not considered the effects of acid catalysis and of solvation, the energy barriers are probably exaggerated.

Conclusion

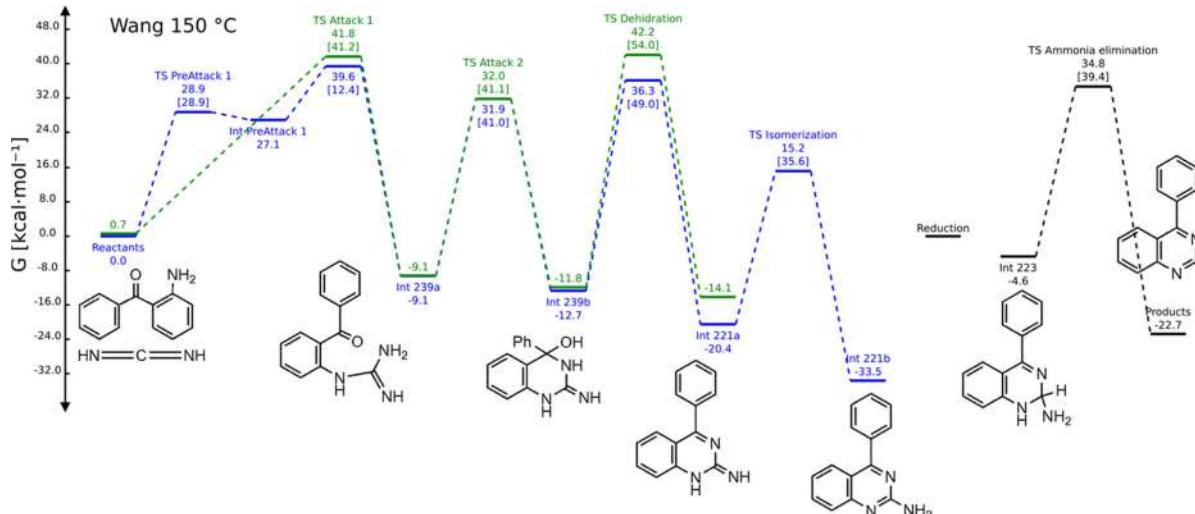
The potential energy curve for the Wang reaction was obtained and the reaction was analyzed in terms of its thermodynamic and kinetic characteristics. Further studies are being carried out to verify the effects of solvation and of acid catalysis. The reduction step, which involves other reactants formed *in situ*, will also be addressed in the future.

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Scheme 1. Gibbs energy curve obtained for the Wang reaction. Two paths differentiated by the orientation of the CN double bond are indicated by the colors blue and green and they converge on the reduction step. Activation Gibbs energies are given for transition states, always in brackets.

Estudo teórico da reação de polimerização do HCN em rotas abiosintéticas para a formação de nucleobases necessários à vida.

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Palavras-Chave: HCN, espontaneidade, nucleobases, evolução química

INTRODUÇÃO

Propostas reacionais na busca da origem química da vida rendeu muito debate na comunidade científica ao longo dos anos. A síntese de nucleobases, a partir do modelo de evolução química, foi amplamente estudada experimentalmente, dando destaque às rotas ciênicas¹. Contudo, esses estudos carecem de um parecer teórico mais aprofundado. Neste trabalho foi investigado e discutido a espontaneidade da polimerização do HCN em rotas prebiótica da síntese de nucleobases (Figura 01).

METODOLOGIA

Foi utilizado a abordagens DFT e Dinâmica Molecular: para os cálculos de frequência para obtenção de ΔG_r foi usado o funcional M06-2X/6-311G+(d,p); para o cálculo de $\Delta G_r/DM$ em solução aquosa foi utilizado o método descrito por Hellwig e Eckert². Para obtenção das barreiras de energia total foram feitos cálculos de IRC e TS com o funcional B3LYP na base 6-31G.

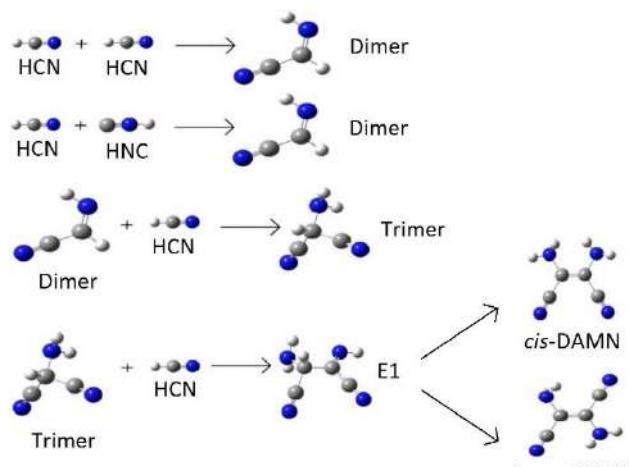


Figura 1: Rota de polimerização do HCN para a formação de diaminomaleonitrila (DAMN), em fase gás.

RESULTADOS

A tabela 1 reúne os resultados termodinâmicos de ΔG_r para as etapas reacionais, a tabela 2 exibe as barreiras de energia total para cada reação.

Tabela 1: Resultados de ΔG_r (em kJ) da rota de polimerização do HCN na temperatura de 298 K e 1 atm.

Reação de Formação	Resultados de ΔG_r em fase gás	Resultados de ΔG_r em solução aquosa
HCN+HCN → Dímero	12,04	2,01
HCN+HNC → Dímero	-40,88	-48,39
HCN + Dímero → Trímero	-35,33	-34,94
HCN + Trímero → E1	0,83	-8,92
HCN + E1 → trans-DAMN	-48,83	-45,23
HCN + E1 → cis-DAMN	-46,43	-49,94

Tabela 2: Resultados de barreira de energia total (em kCal/mol) de cada etapa reacional pelo método B3LYP-6-31G.

Reação de Formação	Barreira de energia total (fase gás)	Barreira de energia total (solução aquosa)
HCN+HCN → Dímero	-	103,0
HCN+HNC → Dímero	35,0	32,0
HCN + Dímero → Trímero	52,0	68,0
HCN + Trímero → E1	88,0	56,0
HCN + E1 → trans-DAMN	29,0	17,5
HCN + E1 → cis-DAMN	30,0	18,0

CONCLUSÃO

Conclui-se que a reação entre monômeros de HCN não resulta na formação do Dímero, no entanto, a reação envolvendo o HNC é espontâneo. Contudo, a molécula de HNC é altamente instável, encontrada somente no espaço. O meio aquoso possui os menores valores de barreira de energia total, exceto para a formação do Trímero.

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XXI SBQT

DESCRÍÇÃO DA CINÉTICA DE DEGRADAÇÃO DE POLUENTES ORGÂNICOS ATRAVÉS DE MÉTODOS DE QUÍMICA QUÂNTICA E DE APRENDIZADO DE MÁQUINA

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Palavras-Chave: *Micro poluentes, Teoria de Estado de Transição, Inteligência Artificial.*

A presença de poluentes orgânicos persistentes no meio ambiente é uma preocupação ambiental, demonstrada também pelas mudanças climáticas globais [1,2]: a persistência desses compostos pode causar efeitos adversos à saúde [3,4].

A constante cinética de uma reação química desempenha um papel fundamental em tecnologias para revelar a eficiência da oxidação/mineralização desses contaminantes emergentes no meio ambiente [5,6]. Nos últimos anos, metodologias experimentais baseado em tecnologias de oxidação avançado (TOA's) tem sido empregada com o objetivo de degradar e/ou mineralizar esses poluentes dos corpos d'água e na atmosfera. A reação do radical hidroxila foi avaliada por nosso grupo em vários trabalhos teóricos para sistemas de quatro corpos, onde estendemos o entendimento da dinâmica reacional para a contribuição do tunelamento quântico, estereodinâmica e roaming [7]. Para ampliar a compreensão do comportamento e destino de compostos mais complexos, as constantes de velocidade desses processos são os parâmetros mais relevantes para estimar sua eficiência. No entanto, medidas da constante cinética da reação por meio de técnicas experimentais são consideradas laboriosas e dispendiosas, limitando a sua aplicação a grupos de pesquisas específicos.

Portanto, a obtenção da constante cinética da reação mediado por processos oxidativos de contaminantes orgânicos em meio aquoso e atmosférico a partir de estimativas teóricas e previsões baseadas em aprendizado de máquina tornam-se vantajosas. Nesta direção destacam-se as propostas desse estudo, como: (i) revelar o mecanismo, cinética e toxicidade do pesticida picloram com o radical hidroxila e (ii) desenvolver protocolos de aprendizado de máquina para fazer a previsão da constante cinética de processos baseado em radicais em ambiente aquoso. Para a primeira proposta do trabalho, são fornecidos resultados da constante cinética, razão de ramificação, tempo de meia-vida,

fotólise e toxicidade do picloram e dos principais produtos de degradação. Na segunda abordagem, nós desenvolvemos uma aplicação web estruturado em um algoritmo de aprendizado de máquina combinado com impressões digitais moleculares para o cálculo automático da constante cinética de processos oxidativos de poluentes orgânicos mediados por radicais OH^- e SO_4^{2-} em fase aquosa e radicais OH^- em fase gás – a plataforma *pySiRC* (*python Simulator Rate Constant*) [8]. Para realizar este estudo, o seguinte fluxo de trabalho foi adotado: coleta de dados, pré-processamento de dados, desenvolvimento de modelo, validação e interpretação de modelo - todos os protocolos para o desenvolvimento de modelos QSAR de acordo com a Organização para Cooperação e Desenvolvimento Econômico (OCDE) [9] e técnicas de ponta foram realizadas. Os resultados mostram que os modelos desenvolvidos têm alta capacidade preditiva – $R^2 > 0.931$ e $RMSE < 0.101$ para o conjunto de treinamento e $R_{ext}^2 = Q_{ext}^2 > 0.639$ e $RMSE < 0.094$ para o conjunto de teste. Espera-se que os resultados apresentados aqui possam estimular e expandir o desenvolvimento de protocolos para a pesquisa em cinética química, por meio de ferramentas teóricas ou *in silico*, com aplicações consistentes na remoção de contaminantes emergentes no meio ambiente.

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INSIGHTS FROM DFT ANALYSIS INTO PALLADIUM-CATALYZED HECK COUPLING BETWEEN 3-BROMO-2-METHOXYLAWSONE AND 1H-1,2,3-TRIAZOLES DERIVATIVES

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Keywords: DFT, Heck Reaction, Naphthoquinones.

Introduction

Palladium-catalyzed coupling reactions between alkenes and aryl halides, known as Mizoroki-Heck reactions, are among the most important methods for the construction of carbon-carbon bonds, and they have been used extensively in the synthesis of natural products¹.

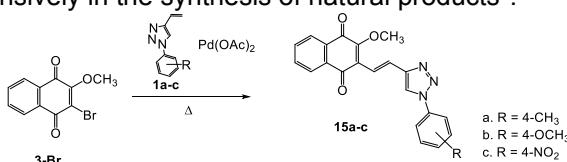


Figure 1. Synthesis of product 15a-c.

In this work, the mechanism of a coupling reaction between 1,4-naphthoquinone and 1H-1,2,3-triazole derivatives in the presence of a Pd^{II} catalyst (experimental data suggest that palladium black - Pd⁰ was not observed at the beginning of the reaction) for the synthesis of a quinone-triazole conjugate (Fig. 1) was investigated.

Methodology

All electronic structure calculations were performed using the functional CAM-B3LYP. The Def2SVP basis set was used for all atoms. Implicit solvation effects were included using IEFPCM, with water as a solvent. The energetic span values, used to have a quicker estimative of the TOF (*turnover frequency*), was calculated using equations (1) and (2)². When the highest transition state appears after the most abundant intermediate in the cycle:

$$\Delta\delta = \Delta E_{TS} - \Delta E_{INTERM} \quad (1)$$

Or, if the highest transition state appears before the most abundant intermediate in the cycle:

$$\Delta\delta = \Delta E_{TS} - \Delta E_{INTERM} - \Delta G_{REAÇÃO} \quad (2)$$

Results and Discussion

The most accepted mechanism for this reaction initiates with the oxidative addition of aryl halide to the active species of palladium. However, Yao et. al³ proposed an alternative mechanism, in which the olefin in the reaction mixture reacts with the Pd catalyst to form intermediate 5b, the so-called palladacycle intermediate (Fig. 2).

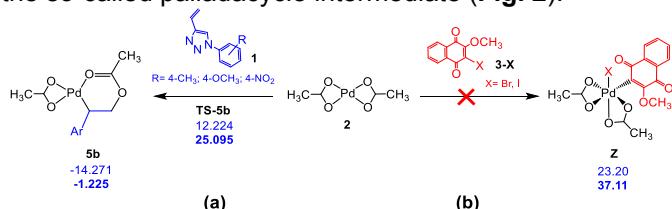


Figure 2. (a) Formation of palladacycle intermediate (5b), as proposed by Yao et al³. (b) Mechanism proposed for the Heck reaction.

As the naphthoquinone addition to Pd(OAc)₂ is much unfavorable, the study of this reaction mechanism was continued considering the coordination of the alkene to the

palladium catalyst in the first step of the process. Both mechanisms converge to a common intermediate (8). Data in Fig. 3 indicate that the most important step in this mechanism is the formation of the C-C bond to form intermediate 11. Other mechanistic alternatives have been investigated from intermediate 8, but it is beyond the scope of this abstract.

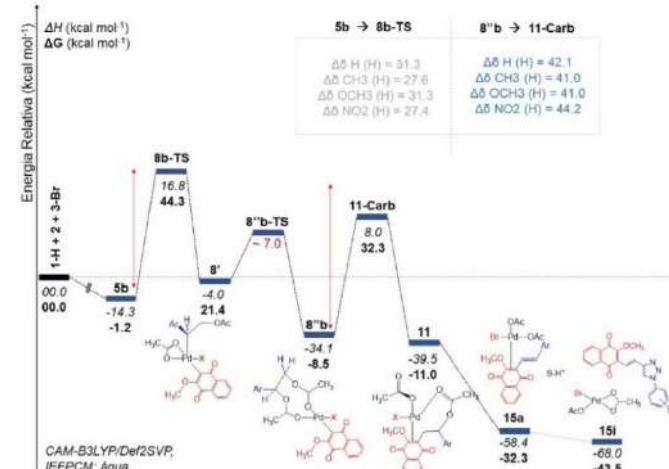


Figure 3. Energy profile of the mechanism proposed with formation of the palladacycle intermediate. Energy span values (kcal mol⁻¹) calculated according to Kozuchi and Shaik².

The main points on the energy map were considered to rationalize the experimental data (Fig. 3). The influence of electron-withdrawing (1-NO₂) and electron-donor substituents (1-CH₃ and 1-OCH₃) in the 4-vinyl-1H-1,2,3-triazoles (1) derivatives was also investigated. According to the Energy Span Model presented by Kozuchi and Shaik², the energy span ($\Delta\delta$) was calculated using the Equation 1 to rationalize the differences observed on the reaction yield. The calculated values showed similar values for $\Delta\delta(H)$, using enthalpy. Experimental data reveal the nitro substituent (28%) shows a lower yield than 1-CH₃ (70%).

Conclusions

The electron-withdrawing groups may activate the olefin. However, the mechanistic study in this work shows that the double bond acts as an electron-donor to the bond in coordination with the palladium atom. In this sense, electron-withdrawing groups would, in fact, deactivate the olefin for the coupling.

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Interconversion mechanisms of PN and PO in the interstellar medium through simple atom-diatom collisions

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Palavras-Chave: astrochemistry, phosphorus, ISM - molecules

Introdução

O elemento fósforo é extremamente importante para a existência da vida como conhecemos, já que desempenha um papel essencial na química de moléculas como ATP, DNA, RNA. Curiosamente, sua abundância estimada no universo é diversas ordens de magnitude menor do que sua abundância em organismos vivos (RIVILLA et al., 2020), o que levanta a importante questão sobre como esse elemento se tornou biologicamente disponível para o surgimento da vida.

Entretanto, a química de moléculas contendo fósforo no meio interestelar ainda não é bem conhecida. Os modelos propostos que tentam elucidar a abundância de moléculas contendo fósforo como PN e PO baseiam-se nos resultados de reações análogas como, por exemplo, as que envolvem NO. Atualmente, foi proposto que PO e PN podem ser os principais constituintes da reserva de fósforo na fase gasosa no meio interestelar (Lefloch et al. 2016).

Metodologia

Neste trabalho foram realizados cálculos utilizando o método *Complete Active Space Self Consistent Field* (CASSCF) e a energia fornecida pelo *Multireference Configuration Interaction* (MRCI) para o estudo das reações N+PO e O+PN (SOUZA; SILVA; GALVÃO, 2021). Essas reações podem ocorrer em dois estados eletrônicos ($^3A'$ e $^3A''$), e ambos foram estudados.

Resultados

Conforme pode ser visto na figura 1, a colisão entre nitrogênio atômico e a diatômica PO resulta em uma estrutura de mínimo angular sem que haja nenhuma barreira em ambos os estados eletrônicos. Essa molécula, também em ambos estados eletrônicos, pode sofrer a perda de oxigênio passando por um estado de transição, levando aos produtos O+PN de maneira exotérmica. Como pode ser visto, a partir do mínimo NPO $^3A'$ existe um caminho de formação dos produtos P+NO que envolve múltiplas isomerizações, sendo uma delas através de uma interseção côncava. Por esse motivo, esse produto deve ser minoritário.

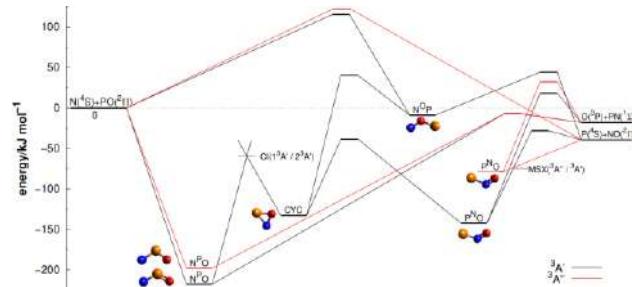


Figura 1 – Diagrama de energia potencial para os estados $^3A'$ (preto) e $^3A''$ (vermelho).

O outro caminho para a dissociação do fósforo seria através de uma abstração do oxigênio do tipo $N+PO \rightarrow NOP \rightarrow P+NO$, porém os cálculos preveem uma barreira elevada de aproximadamente 115 kJ mol⁻¹ para o estado $^3A'$ e 122 kJ mol⁻¹ para o $^3A''$, o que torna esse mecanismo inviável para o meio interestelar.

Conclusão

Os resultados teóricos obtidos corroboram com os valores assumidos nas bases de dados astroquímicas para essas reações e adicionam os valores quantitativos de energia relativos a esse sistema. Portanto, foi possível elucidar diversos aspectos da superfície de energia potencial, incluindo mínimos, estados de transições e cruzamentos. Além disso, foi possível confirmar que N+PO é uma colisão sem barreira de ativação e gera como produto principal O+PN que é cineticamente favorável.

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NONLINEAR OPTICAL PROPERTIES OF C₆₀ FULLERENE DERIVATIVES

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Keywords: Fullerene, Hyperpolarizability, DFT.

INTRODUCTION

The theoretical chemical models can contribute for the designing of novel materials with impact in the areas of the nanoscience and nanotechnology. The modeling of derivatives of C₆₀ fullerene with diethynylsilane oligomers was performed using the density functional theory (DFT). The optimization of the nonlinear response was achieved through the introduction of substituents groups at the end of the oligomers chain (Fig. 1). The results indicate that the hybrid systems show very larger β values.

Early *ab initio* and semiempirical results for the first hyperpolarizability (β) of donor-acceptor diethynylsilane oligomers with increased chain size demonstrated that these systems are potential building blocks for molecular-based material with second-order nonlinear responses [1]. Polydiethynylsilane (PDES) is a π -conjugated polymer incorporating Si that has been theoretically and experimentally characterized as a third order NLO material. Moreover, various derivatives of C₆₀ fullerene show relevant second hyperpolarizability (γ) values according to theoretical studies [2].

METODOLOGY

The geometry optimization was performed using the PBE1PBE hybrid functional with the 6-31G(d,p) polarized basis set. N-methylfulleropyrrolidine (NMFP-n) derivatives were investigated, where n is the diethynylsilane rings number in the oligomer chain (n is equal of 1-10). The dicyanoethenyl (S1) and tert-butyl (S2) are the substituents groups selected in this study. The coupled perturbed Kohn-Shan (CPKS) methodology at the PBE1PBE/6-31G(d,p) level was utilized for the calculation of the static β values of the systems investigated. Also, the polarizability (α) was calculated for the studied systems. All the calculations were performed using the Gaussian 09 program.

RESULTS

Fig. 1.
Optimized
structure of the
S1-NMFP-10
(C106H47N3Si10)
system.



Fig. 2.
Behaviour of β
for the
nonsubstituted
C₆₀ derivatives
versus the
HOMO-LUMO
gap.

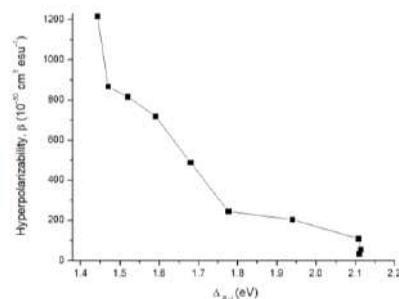


Table 1. PBE1PBE/6-31G(d,p) calculated properties for some substituted C₆₀ derivatives.

	$\alpha\pi$	$\beta\pi$	$\mu\pi$	ΔE_{HL} (eV)	IE (eV)
S1-NMFP-5	2338	1602	5.16	1.913	5.474
S2-NMFP-5	2148	626	10.85	1.640	5.020
S1-NMFP-6	2755	2479	5.99	1.772	5.322
S2-NMFP-6	2508	866	11.44	1.752	5.130
S1-NMFP-7	2876	1886	12.49	1.563	5.129
S2-NMFP-7	2686	1253	11.46	1.506	4.878
S1-NMFP-8	3427	3139	7.33	1.472	5.107
S2-NMFP-8	3159	1141	13.20	1.451	4.819
S1-NMFP-9	3924	4430	5.34	1.400	5.016
S2-NMFP-9	3657	1972	15.70	1.419	4.774
S1-NMFP-10	4231	6293	8.78	1.290	4.917
S2-NMFP-10	3907	2271	16.94	1.470	4.761

NMFP-n derivatives, S1 is the dicyanoethenyl group, S2 is the tert-butyl group, $\alpha/10^{-25} \text{ cm}^3$ (polarizability), $\beta/10^{-30} \text{ cm}^3 \text{ esu}^{-1}$ (first hyperpolarability), μ is the ground state dipole moment (D), Δ is the HOMO-LUMO gap, IP is the ionization potential.

CONCLUSIONS

The C₆₀ derivatives show remarkable β values at the PBE1PBE/6-31G(d,p) level. The introduction of the dicyanoethenyl group into the diethynylsilane oligomer structures results in marked increasing of β (α) among all systems studied. Also, the HOMO-LUMO gap is reduced when the oligomer size is extended. Our results demonstrated that the hybrid materials investigated containing Si might be promising applied in optoelectronics and photonics.

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FACEPE - CAA/UFPE - DQF/UFPE - CENAPAD-SP

Estudo teórico do mecanismo de ação da enzima RTA da Ricina com um ligante análogo ao substrato natural rRNA 28S

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Palavras-Chave: RTA, Dinâmica molecular, Descritor de reatividade.

A Ricinus communis, planta conhecida no Brasil como mamoneira, tem ganhado atenção da indústria, mídia e governos, em razão das propriedades de seus derivados, em especial a ricina e o óleo ricinoleico. Esse último, corresponde 90% do óleo total que é extraído da semente do fruto e apresenta uma importante economia para a indústria química. Já a ricina, é uma potente toxina capaz de inativar de forma eficiente ribossomos eucarióticos. É constituída de duas subunidades, a RTA e a RTB. Funcionalmente a RTB é responsável pelo reconhecimento e internalização da ricina nas células-alvo e a RTA pela catálise da depurinação da adenina 4324 localizada na região *Sarcin-Ricin Loop* do rRNA 28S. Devido a sua citotoxicidade, facilidade de extração e purificação, a ricina é classificada como agente de ameaça biológica de categoria B segundo o Centro de Controle e Prevenção de Doença (CDC), preocupando autoridades mundiais pelo seu potencial uso como arma biológica. Dessa forma, o desenvolvimento de uma antitoxina seria uma importante conquista farmacêutica e biotecnológica. Contudo, a grande dificuldade em projetar inibidores capazes de agir eficientemente como bloqueadores da RTA se atribui a compreensão incompleta do seu mecanismo de reação. Diante do exposto, esse trabalho tem como finalidade obter um maior esclarecimento acerca do mecanismo de ação da RTA, utilizando a Dinâmica Molecular (DM) e os Descritores de Reatividades (DR), baseados na Teoria Funcional da Densidade Conceitual (CDFT), implementados no PRIMoRDiA [1], para monitorar a interação da subunidade catalítica RTA com um análogo do substrato natural. A trajetória de DM revelou as principais ligações de hidrogênio presentes no sítio ativo da RTA entre os resíduos Val81, Arg180 e Gly121 com a adenina alvo do ligante mimético. Além disso, evidenciou a ligação de hidrogênio que ativa a adenina alvo ao longo de toda simulação. Com o estudo de energia de interação, Figura 1, foram identificadas as interações atrativas de estabilização da adenina pelos resíduos Tyr80, Tyr123, Val81, Gly121 e Glu208 e interações repulsivas pelos resíduos Glu177 e Trp211.

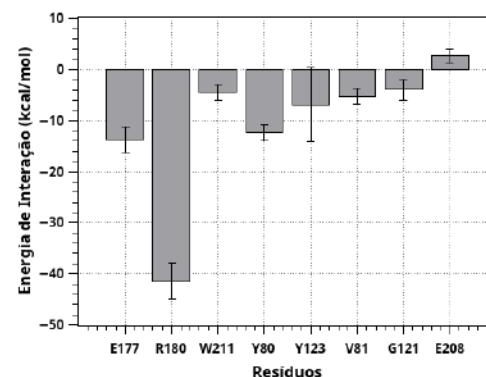


Figura 1- Energia de interação entre os resíduos do sítio ativo da RTA com o ligante mimético.

O resíduo 332 foi identificado como água catalítica do mecanismo. Por fim, as propriedades de reatividades que utiliza a estrutura eletrônica convergida do PM7-MOZYME-COSMO, Figura 2, apontaram para um mecanismo de ação da RTA onde há uma susceptibilidade ao ataque eletrofílico na adenina alvo por meio do resíduo Arg180, uma estabilização da adenina em um empilhamento π entre os resíduos Tyr80 e Tyr123 e uma propensão do Glu177 em ativar a água catalítica doando densidade de elétrons e recebendo um próton.

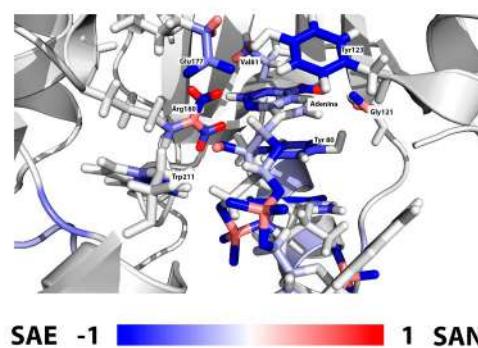


Figura 2- Diferença entre susceptibilidades de ataque eletrofílico e nucleofílico para o sítio ativo da RTA.

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Low-energy positron scattering by tetrachloroethylene (C_2Cl_4) molecule

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Palavras-Chave: Scattering, positron, tetrachloroethylene.

In recent years, positrons have gained increasingly use in diverse applications, ranging from medicine to annihilation spectroscopy [1,2]. For many of these applications, obtaining data of positron collisions is of fundamental importance. Hence, the interest in positron-molecule collisions has grown with the advance of experimental and theoretical methodologies [3,4].

Tetrachloroethylene (Figure 1) is a simple polyatomic molecule and has already been studied on low-energy electron-molecule collision [5]. Experimental realizations on positron collisions with this system indicated a positron-molecule bound state formation [6]. Therefore, theoretical study of positron collisions with tetrachloroethylene may bring new interesting data in comparison with electron-molecule collisions, once there is the change of sign of interaction potential and the absence of the exchange potential. To compute the cross sections of low-energy positron collisions with tetrachloroethylene, Schwinger Multichannel method (SMC) was employed with TZV ++ (2d,p) basis set, in the static plus polarization (SP) approximation. All valence orbitals were used as hole and scattering orbitals. The calculations with 47 MVOs (modified virtual orbitals) as particle orbitals will be labeled as SP-1 and the calculations with 72 MVOs will be labeled as SP-2.

Seeking to obtain a better description of polarization effects, we added p and d-type extra functions centered on chlorine atoms and three sets of MVOs as particle orbitals. The calculations with 47 MVOs will be labeled as DIF-1; with 72 MVOs will be labeled as DIF-2 and with 79 MVOs will be labeled as DIF-3.

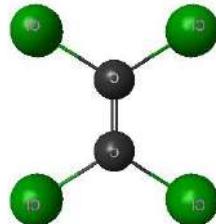


Figure 1. Structure of studied tetrachloroethylene

We will present theoretical results of integral and s-wave elastic cross sections for energies ranging from 10^{-6} to 10 eV. From figure 2, we could identify the Ramsauer-Townsend (RT) minimum in all calculations. Analyzing the scattering length (SL) data (Table 1) and eigenphase, we observed the existence of a positron-molecule bound state formation for DIF-3.

3 calculations. This shows the importance of the inclusion of diffuse functions in our basis set to better describe the polarization process.

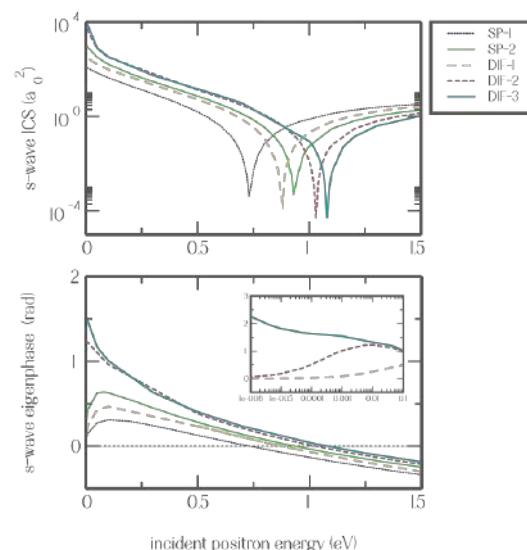


Figure 2. s-wave cross section (top) and respective eigenphase (bottom) obtained with different schemes of polarization

Label	SL(a_0)	RT(eV)
SP-1	-5.9	0.73
SP-2	-18.9	0.93
DIF-1	-9.8	0.88
DIF-2	-209.4	1.03
DIF-3	4517.6	1.08

Table 1. Scattering length and Ramsauer-Townsend minimum for each calculation labeled as SP-1 to DIF-3

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Computational study of chemical bonds in carbon and silicon tetrafluorides interacting with NH₃ and PH₃

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Keywords: Tetrel Bonds, Overlap Properties, QTAIM Properties.

Introduction

Over the last few years, different computational studies have been carried out concerning Lewis acids and bases interactions [1]. This concept of acids and bases was expanded by Lewis theory, which classified acids as chemical species that accept electron pairs and bases as chemical species that donate electron pairs. A significant type of interaction is the tetrel bond, which is defined as an interaction between a Group 14 element acting as a Lewis acid center and an electron-rich species that will play the role of the Lewis base [1]. This interaction occurs because of the presence of a positive region on the electrostatic potential of the Lewis acid, which is called σ -hole [2]. Molecular systems of interest that present unconventional chemical bonds are carbon, silicon, and germanium tetrafluorides interacting with one or two NH₃, AsH₃, or PH₃ molecules. Different chemical bond analysis methodologies can be applied to study this type of interaction. In the present work, we report the comparison of our chemical bond overlap (OP) model [3] with the Quantum Theory of Atoms in Molecules (QTAIM) model. In this perspective, the studied systems were Y…XF₄…Y, where X = C or Si, and Y = NH₃ or PH₃.

Methodology

The geometries of the studied molecular systems were optimized at the ω B97X-D level with the aug-cc-pVQZ base set using the GAMESS program. The localized molecular orbitals necessary to the OP model were obtained using the Pipek-Mezey method. The overlap properties (overlap repulsion J_{OP}^{intra} , and density ρ_{OP}) were calculated using our ChemBOS software. The QTAIM analysis was performed using the Multiwfn software to calculate the bond critical points (BCP) properties (electron densities ρ_{BCP} , and Laplacian $\nabla^2\rho_{BCP}$ of density at the BCP).

Results

The DFT was used to perform equilibrium geometry calculations, calculation of wave function, location of molecular orbitals, analysis of overlap properties, and topological analysis of the 4 molecular systems studied in this work. In Table 1 is possible to see the results of these chemical bonding properties for these interactions, obtained through the OP models and the QTAIM model. It is possible to observe, in Table 1, that the $\nabla^2\rho_{BCP}$ values for C…N and C…P interactions (entries 1 and 2) are negative, indicating a charge concentration in the chemical bond region. Despite that, QTAIM descriptors do not differentiate these two systems. On the other hand,

high J_{OP}^{intra} values point to a chemical bond with charge concentration. Also, OP descriptors differ in these interactions, pointing to a more expressive charge concentration in the C…P interaction. Si…N interaction exhibits QTAIM descriptors related to an electrostatic behavior. Additionally, Si…N exhibits weak interaction behavior, compared with the other studied systems, for both QTAIM and OP results.

Table 1. Calculated chemical bonding properties: Bond distance R (in Å), Intra-overlap repulsion J_{OP}^{intra} (E_h), and density ρ_{OP} (e), electron density ρ_{BCP} (e/a_0^3) and Laplacian $\nabla^2\rho_{BCP}$ (e/a_0^5) of density at the BCP.

System	R	J_{OP}^{intra}	ρ_{OP}	ρ_{BCP}	$\nabla^2\rho_{BCP}$	
1	CF ₄ …(NH ₃) ₂	1.65	6,15	0.50	0.18	-0.22
2	CF ₄ …(PH ₃) ₂	1.83	19,44	1.06	0.18	-0.21
3	SiF ₄ …(NH ₃) ₂	1.94	5,73	0.54	0.08	0.28
4	SiF ₄ …(PH ₃) ₂	2.41	1,32	0.20	0.06	0.05

In Figure 1, it is observed that the overlap density maps follow the trends pointed out in Table 1.

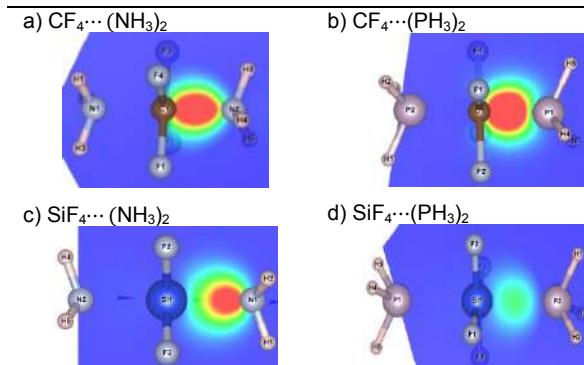


Figure 1. Overlap and QTAIM properties for the studied acid-base interaction. Color maps in RGB in the range of 0 – 0.06 e/a_0^3 .

Conclusions

The overlap properties support the QTAIM results. More analyses are being made addressing the C–F spectator bonds under the light of QTAIM, OP, and Local Vibrational Modes [4] theory to understand the electronic situation of Lewis acid center when interacts with different bases.

Acknowledgments

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Estudo comparativo das reações unimoleculares de bis(metóxi-metil) éter e trimetóxi-metano

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Palavras-Chave: éteres de oximetíleno, dissociações, combustão.

Introdução. A busca por alternativas aos combustíveis fósseis é de interesse global, não somente por razões econômicas, mas principalmente pela possibilidade de se alcançar processos mais limpos de combustão. Neste contexto, é sugerida a adoção de éteres de oximetíleno (OME_n). Acetais como o bis(metóxi-metil) éter e trimetóxi-metano (OME2 e TMM, respectivamente, **Figura 1**) são incluídos neste grupo e se mostram potenciais candidatos a combustíveis ou aditivos.^{1,2}

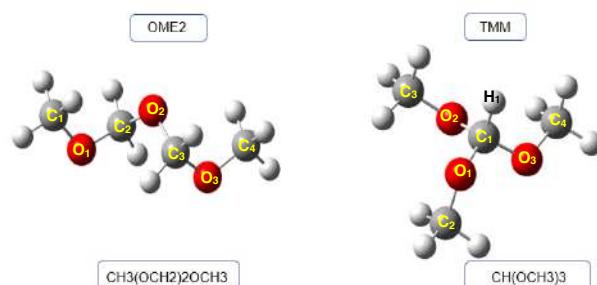


Figura 1. Estruturas de bis(metóxi-metil) éter (OME2) e trimetóxi-metano (TMM).

Sua combustão não gera fuligem, as emissões de CO NOx são relativamente baixas. Apesar destas vantagens, pouca informação físico-química está disponível acerca das reações elementares destes combustíveis. Assim, este trabalho foi desenvolvido com claro objetivo de determinar propriedades termodinâmicas e cinéticas de reações químicas desses dois isômeros, OME2 e TMM.

Métodos Computacionais. Cálculos teóricos foram realizados com o programa Gaussian, G09, em nível M06-2X/aug-cc-pVTZ, incluindo otimizações de geometrias, previsão de frequências vibracionais e caminhos de reação.

Resultados e Discussão.

Inicialmente foi realizada a busca pelos pontos estacionários caracterizados como mínimos globais que representam as estruturas de OME2 e TMM a partir de uma análise conformacional, na qual ângulos diedros selecionados foram sistematicamente modificados gerando chutes iniciais que foram submetidos ao procedimento de otimização de geometria. Algumas conformações distinguíveis reveladas por esta análise são apresentadas na **Tabela 1**. Para o OME2 foram usados os ângulos C₁O₁C₂O₂ (D1), O₁C₂O₂C₃ (D2), C₂O₂C₃O₃ (D1) e O₂C₃O₃C₄ (D1) e para o TMM foram selecionados os diedros H₁C₁O₁C₂ (D1), H₁C₁O₂C₃ (D2) e H₁C₁O₃C₄ (D3).

Tabela 1. Análise Conformatinal de OME2 e TMM ângulos diedros são dados em graus e a diferença de energia, ΔE , em kcal/mol.

#conf	D1	D2	D3	D4	ΔE
OME2#1	65.75	70.62	70.62	65.75	0.00
OME2#2	-63.10	-67.43	179.49	-68.24	2.48
OME2#3	-179.44	64.65	159.20	-65.45	4.33
OME2#4	65.89	179.23	179.23	65.89	5.08
TMM#1	-178.54	-54.27	-56.67	-	0.00
TMM#2	139.69	174.00	55.55	-	2.52
TMM#3	-146.43	-146.43	-146.43	-	7.48

Pontos de sela foram localizados para os canais de eliminação de H₂ para as conformações de menor energia de OME2 e TMM. A conexão entre reagentes, pontos de sela e produtos foi confirmada por cálculos de coordenada de reação intrínseca. Além dos canais de desidrogenação, foram investigados os canais de dissociação de átomos de hidrogênio, radicais CH₃ e CH₃O.

Coeficientes de velocidade foram calculados para as etapas elementares mais relevantes ao mecanismo de decomposição térmica de OME2 e TMM, mostrando resultados compatíveis com a de outros compostos da mesma classe. Por exemplo, os coeficientes de velocidade para a dissociação de radicais CH₃ a partir do TMM são expressos por: $1.05 \times 10^{11} (T^{2.05}) \text{ EXP}(-89.09/RT)$, em s⁻¹ e energia de ativação em kcal/mol, semelhantes aos observados para dissociações de dimetil éter e dimetóxi metano.

Conclusões.

Este estudo permitiu identificar os mínimos globais para os isômeros bis(metóxi-metil) éter e trimetóxi-metano e seus caminhos de reação. A cinética de das reações unimoleculares mostra resultados satisfatórios, podendo contribuir para o desenvolvimento de seus modelos de combustão.

Agradecimentos. O presente trabalho foi realizado com apoio da FAPERJ, CNPq e da UFRJ.

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Positron binding to atoms and molecules: Machine learning studies

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Palavras-Chave: positron, bound-states, machine learning

Slow positrons are able to bind to atoms and molecules, forming short-lived weak complexes [1]. The bonding mechanism is quite complicated, resulting in huge obstacles to ab initio calculations. Binding energies ϵ_b have been measured for some polar and few non-polar molecules [1]. For atoms from Z=1 to 92, a source of systematic ab initio calculations exists, though the results seem to be subject to random errors [2]. Sophisticated many-body calculations are restricted to a few systems.

In this work we resort to artificial intelligence, more particularly, machine learning (ML) techniques, to handle experimental results for molecules and systematic theoretical results for atoms. The interest is twice: i) To make predictions of binding energies for unknown systems as well as to correct possibly wrong reported values; ii) To correlate the binding mechanisms to properties of the target atom or molecule. In special for the last goal, the synergistic interaction between human intuition and the machine in searching for hidden correlations becomes an invaluable tool.

Particularly, it was found that the ionization potential E_i of the targets plays the role of a repulsive short-distance potential that regularizes the attractive polarization potential for non-polar molecules and atoms [3,4]. For molecules [3], a formula for ϵ_b was found in terms of E_i and the polarizability α , namely,

$$\begin{aligned} \epsilon_b(\alpha, E_i) = & C_1 \text{abs}\left(E_i \ln E_i - \frac{E_i \alpha}{E_i - \alpha}\right) \\ & + C_2 \text{abs}\left(\frac{E_i}{\sqrt{\alpha}} - \frac{1}{E_i(\alpha - E_i)}\right) \\ & + C_3 \text{abs}\left(\frac{E_i \alpha}{\alpha - E_i} - \frac{e^{E_i}}{\alpha^{1/3}}\right) + C_4, \quad (1) \end{aligned}$$

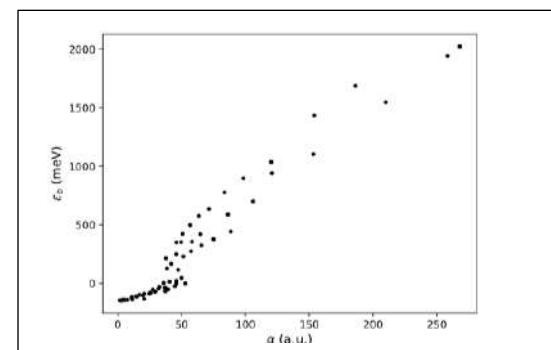
where $C_1 = 0.07706$, $C_2 = -0.96591$, $C_3 = 0.15305$, and $C_4 = 0.004247$, in a.u., and "abs" means the modulus of the

which yields the results in the following table.

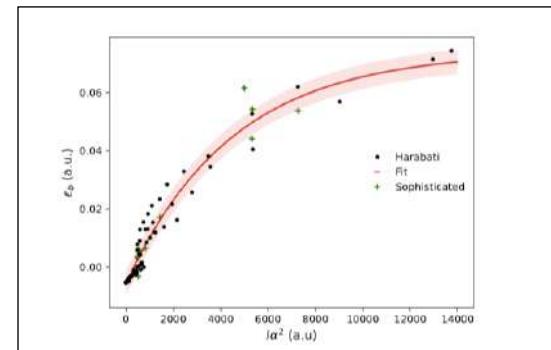
TABLE I. Binding energies (meV) for apolar molecules. E_i in meV and α in Å^3 . Expt stands for experimental results from Refs. [33–35]; DYS refers to fitting to Eq. (5) in Ref. [33]; SG refers to Ref. [27]; TW means “this work.” Molecular properties data taken from the experimental sources [33–35].

Molecules	Formula	E_i	α	Expt	DYS	SG	TW
Butane	C_4H_{10}	10.6	8.1	35	31	26	39
Pentane	C_5H_{12}	10.4	10.0	60	54	56	54
Hexane	C_6H_{14}	10.2	11.8	80	77	87	75
Heptane	C_7H_{16}	9.9	13.7	105	100	117	105
Octane	C_8H_{18}	10.0	15.5	115	123	144	119
Nonane	C_9H_{20}	10.0	17.4	145	146	168	144
Dodecane	$\text{C}_{12}\text{H}_{26}$	9.9	22.9	220	214	222	223
Hexadecane	$\text{C}_{16}\text{H}_{34}$	9.9	30.3	310	306	264	308
Ethylene	C_2H_4	10.5	4.2	20	-17	20	
Cyclopropane	C_3H_6	9.9	5.7	10	1	10	
Cyclohexane	C_6H_{12}	9.9	11.1	80	68	83	
Benzene	C_6H_6	9.3	10.4	150	149	148	
Naphthalene	C_{10}H_8	8.2	16.6	300	296	301	
2,3-butandione	$\text{C}_4\text{H}_6\text{O}_2$	9.3	8.2	77	92	79	
Other molecules and predictions							
Carbon disulfide	CS_2	10.1	8.7	75	98	71	
Hexafluorobenzene	C_6F_6	9.9	9.8		141	84	
Phosphorus chloride	Cl_3P	9.9	12.8		89	98	
Cyclodecane	$\text{C}_{10}\text{H}_{22}$	10.0	18.5		160	159	
Bicyclo[2.2.1]heptane	$\text{C}_{10}\text{H}_{16}$	9.4	17.7		151	215	
1,3,5-hexatriene	C_6H_8	8.3	11.2		69	71	
Carbon tetrabrom	CBr_4	10.3	15.3		120	123	

In the case of binding to atoms [4], a new and simple descriptor was found, namely $I_p \alpha^2$ ($I_p = E_i$), which nicely separates the bound and unbound cases reported in the source. The original $\epsilon_b \times \alpha$ distribution, already cleaned from points with probably very large errors, shown below



is replaced by a smoother* distribution $\epsilon_b \times I_p \alpha^2$,



which is fitted to the simple formula,

$$\epsilon_b(X) = A - B \exp(-CX), \quad X = I_p \alpha^2$$

which we claim to correct many wrong values and also predicts binding to the Rf atom, with $\epsilon_b = 882$ meV.

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[Ru(bpy)₂(HAT)]²⁺ as potential photosensitizer in Photodynamic Therapy

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Keywords: DFT, Photophysics, Photodynamic Therapy.

Introduction

Photodynamic Therapy (*PDT*) is a good alternative to cancer treatment. The technique consists of using a photosensitizer (*PS*) that is applied to the blood stream and, after a waiting period is irradiated in the visible spectrum of light and undergoes several possible reactions. Porphyrins and its derivatives are the most common type of *PS* but there are many studies with several classes of molecules and ruthenium complexes are amongst the most promising. The complex [Ru(bpy)₂(HAT)]²⁺ is an interesting molecule which presents the light-switch effect (only reactive in the presence of light) and can intercalate with the DNA of the cancer cells.

In this work we have performed a *DFT* study to elucidate the photophysics/photochemistry and the thermodynamics of the reactions of the complex with oxygen species, nitric oxide and Guanosine-5'-monophosphate nucleotide (*GMP*).

Methodology

Time-independent and time-dependent Density Functional Theory (*DFT*) were employed using the hybrid functional PBE0 and the valence triple-zeta basis def2-TZVP(-f). Several geometry optimizations of various states were performed, and the spectra of these states were evaluated. The solvent effect was evaluated using the continuous method (*CPCM*) for the thermodynamic reactions. Zeroth order regular approximation (*ZORA*) formalism was used to account for relativistic effects in the Spin-Orbit Coupling (*SOC*) calculations. The photophysics of the complex was investigated by computing the fluorescence lifetime and the intersystem crossing rates.

Results and Discussion

The geometry optimization calculations showed that the structural differences observed between the ground and excited states of the complex are small with the main differences in the dipole moment observed in water solution indicating that they have quite different polarities.

Table 1: Phosphorescence results in water

State	SOC (cm ⁻¹)	S ₁ /T _n	k _{ISC} (s ⁻¹)
T ₁	49.40		-
T ₂	434.38		5.18x10 ¹¹
T ₃	419.87		1.08x10 ¹¹

The absorption spectra calculations showed three

triplet excited states (T₁, T₂ and T₃) with lower energy than the first singlet excited state (S₁). The calculated SOC was 10 times greater between S₁ with T₂ and T₃ than S₁ with T₁. The fluorescence rate for the S₁ was 1.87×10⁵ s⁻¹, which is small for fluorescence decay, meaning that the S₁ state is not emissive by fluorescence. The computed phosphorescence rates are several orders of magnitude greater than the fluorescence rates which indicates the possible decay mechanism for the complex.

Table 2: Thermodynamics of possible reactions

	Reaction	ΔG _{sol} ^c
1	$^3PS^{2+} + ^3O_2 \rightarrow ^2PS^{*3+} + ^2O_2^-$	-59.2
2	$^3PS^{2+} + ^2NO^\bullet \rightarrow ^2PS^{*3+} + ^3NO^-$	-50.4
3	$^3PS^{2+} + ^2NO^\bullet \rightarrow ^2PS^{*3+} + ^1NO^-$	-15.7
4	$^3PS^{2+} + GMP^{2-} \rightarrow ^2PS^{*3+} + ^2GMP^{*3-}$	-2.0
5	$^3PS^{2+} + GMP^{2-} \rightarrow ^2PS^{*+} + ^2GMP^{*-}$	-92.6
6	$^3PS^{2+} + GMP^{2-} \rightarrow PS^{2+}(S_0) + ^3GMP^{2-}$	-31.7
7	$^3PS^{2+} + ^3O_2 \rightarrow PS^{2+}(S_0) + ^1O_2$	-13.8

Electron-transfer reactions (1-5) are favorable with 5 being the oxidation of *GMP* which indicates that the complex can photo-oxidize DNA. Reactions 6 and 7 are energy transfer processes and show the possible type 1 mechanism via singlet oxygen. Nitric oxide species generation is also favorable which has interesting applications because of the possible formation of azanone (HNO).

Conclusion

The complex [Ru(bpy)₂(HAT)]²⁺ was studied by *DFT* calculations. Structural parameters were similar, but the polarities were quite different between ground and excited states in gas phase and water solution. The phosphorescence rates are greater than the fluorescence rates indicating a possible decay mechanism. Thermodynamics of the reactions showed that the complex can act via both type 1 and type 2 mechanisms, which is according to the literature for HAT ruthenium complexes.

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Reactivity of three different bioactive molecules through a density functional theory study

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Keywords: Density functional theory, Condensed to atoms fukui indexes, Local chemical softness.

The functionalization method consists in the adsorption of molecules on a material surface in order to change its properties for different types of applications, since electronic devices to biomaterials. For biomaterials this process is very important, once that it can increase the biocompatibility between a material surface and the human body, besides other properties as possible increases in the antibacterial properties of the surface. Trino et al studied the adsorption of different bioactive molecules (3-(4aminophenyl) propionic acid (APPA), (3-aminopropyl) trimethoxy silane (APTMS) and 3-mercaptopropionic acid (MPA)) on a TiO₂ surface [1].

In this study it was found that the molecules have some preferential sites to interact with the substrate, but the reason for that behavior is not well understood. In this way, the present study proposes a density functional theory (DFT) analysis of the reactivity of the three bioactive molecules with a (TiO₂)₃ nanocluster (and a hydroxylated version of the same nanocluster) based in the work of Qu et al, seeking to have a better comprehension of the adsorption process of these molecules on TiO₂.

For that a DFT study was proposed, with a B3LYP hybrid XC level of theory for all the structures selected and the 6-31G(d,p) basis set for the bioactive molecules and the LANL2DZ basis set for the clusters. A fully optimization of the molecules structures and the (TiO₂)₃ hydroxylated nanocluster was performed. The obtained optimized structures were submitted to calculations aiming the seeking to obtain the Condensed to Atoms Fukui Indexes (CAFIs), the map of the electrostatic potential (MEP) and the local chemical softness (s) of the structures.

The CAFIs specify which sites are more prone to interact with electrophilic (f-) and nucleophilic (f+) agents, while the local chemical softness enables the evaluation of which of the nucleophilic/electrophilic sites of a structure are more susceptible to interact with other structure electrophilic/nucleophilic site. Combined with the MEP, that allows the prediction of how two structures will interact due the electrostatic potential, these three descriptors can be used to predict and explain the process of interaction of the bioactive molecules with the (TiO₂)₃.

The CAFIs are calculated from differences between the electronic population of a molecule after the insertion and removal of one electron of the system, what can be calculated as:

$$f_k^+ = q_k(N + 1) - q_k(N)$$

$$f_k^- = q_k(N) - q_k(N - 1)$$

Where $q_k(N + 1)$, $q_k(N - 1)$ and $q_k(N)$ are the electronic population of the k -th atom of the cationic, anionic and neutral species.

Equations 3 and 4 illustrate how the local chemical softness are estimated:

$$s_k^n = S f_k^n, \text{ for } n = + \text{ or } -$$

$$S = \frac{1}{IP - EA}$$

Where IP and EA represent the ionization potential and electron affinity of the molecule

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Long Range Parameter Optimization For The Description Of Potential Energy Surfaces Using Density Functional Theory

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Palavras-Chave: Long-Range Parameter, Potential Energy Surface, Density Functional Theory.

Introduction

One of DFT's current weaknesses is a reliable description of Potential Energy Surfaces due to a lack of suitable exchange-correlation functionals. In general, nth order Møller-Plesset's Perturbation Theory (MPn) or other post-Hartree-Fock methods are used in these cases [1].

A particular class of DFT functionals known as long-range corrected (LRC) hybrid density functionals contains a range separation parameter ω that splits and modulates short- and long-range interactions [2]. This parameter could, in principle, be tuned to fit an existing DFT PES using optimization algorithms. This work evaluates this possibility in the hope of obtaining similar results to MP4 while requiring less computational time.

Methodology

The system whose PES was studied in this work consists of a hydrogen peroxide molecule (H_2O_2) and a krypton atom (Kr) [3]. Only the dihedral angle θ and the distance R between the Kr atom, and the O-O bond's midpoint were the variables of interest of our PES scan.

The reference calculation level was the MP4 /aug-cc-pVTZ basis set with the counterpoise correction to avoid the basis set superposition error [3]. The DFT level calculations also used the same basis sets, and the ω B97XD, the LC-BLYP, and the LC- ω PBE functionals [2] were tentatively optimized.

For the ω optimization itself, a Python program was developed to calculate, compare and tune the long-range functional to minimize the discrepancy between the reference and DFT PESs. Two error metrics were tested in this work: Maximum Absolute Error (MaxAE) and Mean Square Error (MSE), however optimization via MaxAE minimization produced results no better than via MSE minimization.

Results

The functionals had an excellent overall performance: in particular, ω B97xd had the best fit

to the reference PES after the optimization. The non-optimized ω B97xd under bound the system [1], and that underbinding was corrected during ω optimization.

LC-BLYP had a mildly successful optimization. Unlike ω B97xd and other LRC functionals [1], it overbound the system. LC- ω PBE showed the worst results in study and this is attributed to the absence of dispersion corrections in this functional.

The total computation time for MP4 was approximately 47 hours and 52 minutes, while DFT calculations were done in 42 hours and 30 minutes, on average, representing a slightly better time performance.

Conclusions

With all results and drawbacks considered, the optimized LRC-DFT using the ω B97xd functional is the best alternative to MP4 among the alternatives exploited in this study.

On the other hand, this research paves the way for different functionals, minimization algorithms and molecular systems to be studied in the future under the same goal of ω optimization for PES scans.

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Estudos computacionais da poli(N-isopropilacrilamida) em solução aquosa de glicerol

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Palavras-Chave: polímeros termodinâmicos, PNIPAm, dinâmica molecular.

Polímeros inteligentes são materiais que sofrem alterações nas suas propriedades em resposta a estímulos específicos provenientes do ambiente. Dentre esses estímulos destacam-se as mudanças de temperatura, pH, força iônica, presença de osmólitos e muitos outros. Esses materiais desempenham um papel importante em diversas áreas, tais como, biomédica, biotecnológica, nanotecnológica, entre outras. A amplitude das aplicações tecnológicas dos polímeros inteligentes depende da possibilidade de ajustar, por exemplo, sua temperatura de transição para desenvolvimento de novas tecnologias. [1-3]

Os polímeros termodinâmicos apresentam uma transição de fases passando de uma estrutura de nôvelo aleatório para globular quando submetido a pequenas alterações de temperatura (T) próximas à temperatura consoluta inferior (LCST). A Poli(*N*-isopropilacrilamida) (PNIPAm) é o polímero inteligente mais estudado nas últimas décadas. Esse polímero apresenta LCST de, aproximadamente, 32 °C. O fato dessa temperatura ser próxima à temperatura corporal indica sua potencial aplicação em sistemas de *drug* e *gene delivery*. [3,4]

A Poli(*N*-isopropilacrilamida) é um polímero de, aproximadamente, 50 anos. Durante esse tempo muitos trabalhos experimentais e computacionais foram propostos. Entretanto, ainda não há um consenso sobre como ocorre e o como é desencadeada essa transição de fases. [5] Dentre algumas das hipóteses destacam-se duas. A primeira, defende que o colapso é puramente hidrofóbico, ou seja, é de natureza entrópica. Por outro lado, a segunda, defende a ideia de um efeito cooperativo com parcelas entrópicas e entálpicas. Com isso, estudos computacionais são necessários para um melhor entendimento deste fenômeno através de um ponto de vista microscópico do comportamento da PNIPAm.

A presença de osmólitos (e.g. glicerol) altera a LCST, como reportado por Venkatesu *et al.* [3] e auxilia na estabilização do estado globular do polímero.

Nesse contexto, esse trabalho foram conduzidos estudos de dinâmica molecular *all-atom* de uma cadeia atáctica de PNIPAm com 32 monômeros utilizando o campo de forças CHARMM36 para descrever os parâmetros ligados e não ligados do polímero e do glicerol. A cadeia foi solvatada com moléculas de água TIP4P/2005. Dois sistemas foram analisados (i) PNIPAm em água e (ii)

PNIPAm em uma solução aquosa de glicerol 0,5 mol/L. Esses sistemas foram submetidos a uma série de simulações com diferentes T, em uma faixa de 270-330 K.

Para validação dos parâmetros utilizados, o raio de giro (R_g) foi monitorado para todas as T (Fig. 1).

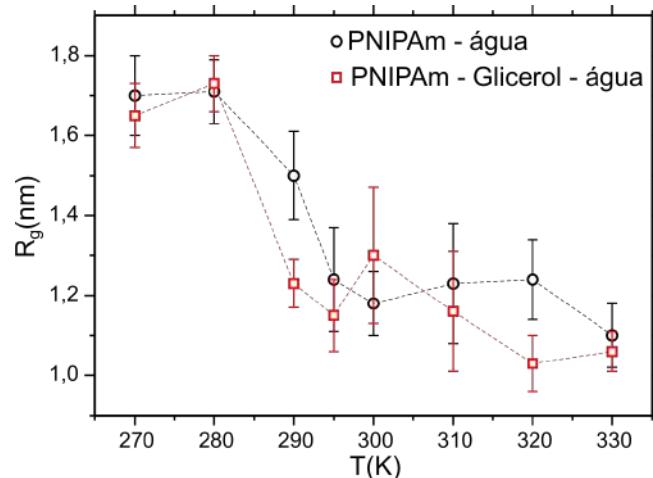


Fig. 1: Raio de giro em função da T.

A análise estrutural do polímero reproduz o que é observado experimentalmente. Para a cadeia em água pura observa-se uma transição de fases entre 295-300K, enquanto para o polímero em solução aquosa de glicerol observa-se uma diminuição da temperatura de transição que ocorre entre 280-295K.

Outras análises foram propostas para verificar a influência das interações polímero-polímero (PP), polímero-água (PW), polímero-glicerol (PG) e glicerol água (GW). Foram analisados o número de ligações de hidrogênio entre os pares mencionados acima. Além disso, foi calculado o número de moléculas nas vizinhanças do polímero utilizando a distribuição radial PW, PG e GW.

Não foram detectadas grandes alterações no perfil de hidratação e ligações de hidrogênio pela presença de glicerol no sistema. Entretanto, analisando as integrais de Kirkwood-Buff, nota-se uma modificação na preferenciabilidade entre PW mais pronunciada na presença de glicerol em função de T.

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Entalpias de formação para compostos de iodo obtidas exclusivamente através de métodos DFT

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Palavras-Chave: *Iodo, Entalpia de Formação, Teoria do Funcional de Densidade.*

INTRODUÇÃO

O iodo^[1] é um elemento fundamental no desenvolvimento corpóreo e auxilia no tratamento do carcinoma papilífero da tireoide. Marinho e Leal^[2] verificaram o desempenho da teoria G3(MP2)/B3-SBK, para o cálculo de entalpia padrão de formação, de um conjunto de 41 compostos de iodo. O desvio médio obtido foi de 9,65 kcal.mol⁻¹ em relação aos dados experimentais. Andrade e colaboradores^[3] realizaram um estudo paralelo para verificar o desempenho de métodos DFT (combinado ao uso de pseudopotenciais) e MP2 para um subconjunto de 33 desses compostos. Esse trabalho mostra o desempenho de diferentes funcionais e conjuntos de base para o mesmo conjunto de 41 compostos de iodo previamente selecionados.

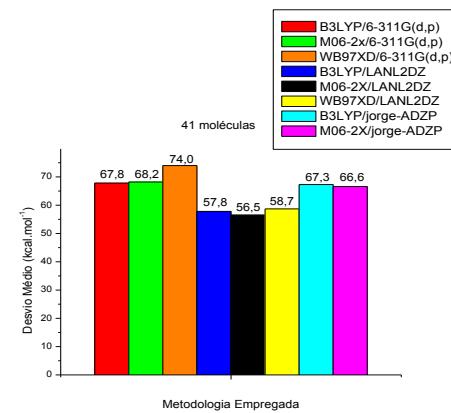
METODOLOGIA

Este trabalho limitou-se ao cálculo de entalpia padrão de formação, em fase gasosa, de 41 moléculas, a saber: C₂H₄CII, Isômeros C₇H₇I (iodo-metil-benzeno, 1-iodo-2-metil-benzeno, 1-iodo-3-metil-benzeno, 1-iodo-4-metil-benzeno), Isômeros C₁₀H₇I (1-iodonaphtaleno, 2-iodonaphtaleno), C₃H₇I, C₃H₅IO, Isômeros C₃H₅I (3-iodo-1-propeno, (E)-1-iodo-propeno, (Z)-1-iodo-1-propeno), C₄H₇IO, Isômeros C₇H₅IO₂ (ácido-2-iodobenzóico, ácido-3-iodobenzóico, ácido-4-iodobenzóico), C₂H₃F₂I, C₂H₂F₃I, C₂H₃IO, C₇H₅IO, C₆F₅I, C₂H₅I, F₅I, HI, BrI, F₇I, ClI, FI, C₆H₅I, CH₃I, C₂H₅IO, C₄H₉I, CF₃I, ISI_H, INO, CIN, BH₂I, CIN₃O₆, H₃ISi, CH₃IS e C₂H₃IN₂O₄. Os dados experimentais foram obtidos na WebNIST^[4]. A entalpia padrão de formação (ΔH_f°) foram obtidas mediante uso de três funcionais (B3LYP, M06-2X e WB97XD) e três conjuntos de base (6-311G(d,p), LANL2DZ, jorge-ADZP, a 298,15 K, conforme procedimento padrão encontrado na literatura^[5]. Todos os cálculos foram realizados com o software Gaussian 09W^[6].

RESULTADOS & DISCUSSÃO

A Figura 1 mostra os desvios médios dos erros obtidos, entre o resultado experimental e calculado, para cada metodologia estudada.

Figura 1: Desvio médio da Entalpia de Formação ($\Delta_f H^\circ$ exp.) dos erros ($\Delta_f H^\circ$ exp. – $\Delta_f H^\circ$ calc.) alcançados para cada metodologia avaliada.



O melhor desempenho foi obtido combinando os funcionais com o conjunto de base LANL2DZ, isso ocorreu devido a redução nos erros de alguns sistemas com a mudança do conjunto de base, por exemplo, 1-iodo-4-metil-benzeno (C₇H₇I), que o erro de 53,5 (B3LYP), 62,6 (M06-2X), 66,5 (WB97XD) com o conjunto 6-311G(d,p) diminuiu para 8,4 (B3LYP), 26,6 (M06-2X), 22,2 (WB97XD) com o conjunto LANL2DZ.

CONSIDERAÇÕES FINAIS

O conjunto de base LANL2DZ apresentou os melhores resultados em comparação ao conjuntos 6-311G(d,p) e jorge-ADZP, para os 03 funcionais testados. Nitrocompostos, como Iodotrinítrometano CIN₃O₆ e iodo-1,1-dinitrietano C₂H₃IN₂O₄, apresentaram altos desvios em todas as metodologias testadas.

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Elaboração de protocolo para design teórico de sistemas contendo íons lantanídeos

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Palavras-Chave: luminescência, lantanídeos, LUMPAC

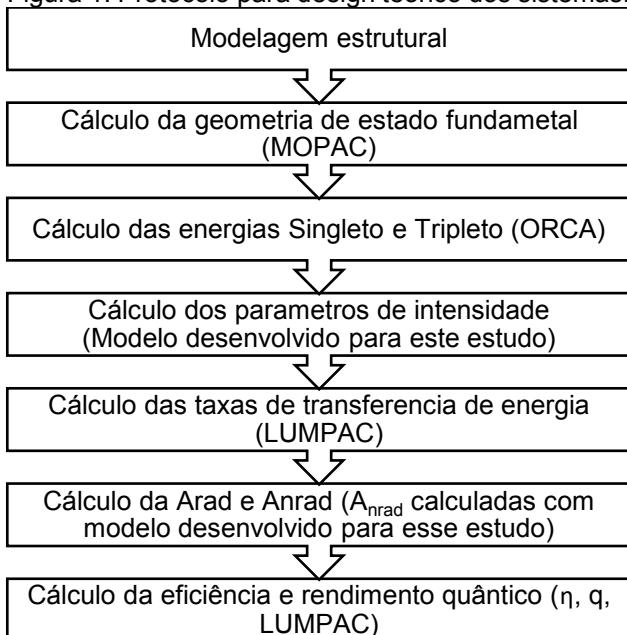
INTRODUÇÃO

Grupos de pesquisa vem alocando esforços consideráveis para o desenvolvimento de novos dispositivos moleculares conversores de luz (DMCLs) cada vez mais eficientes utilizando sistemas contendo íons lantanídeos. Por não existirem um conjunto completo de expressões analíticas para o cálculo dos parâmetros de Intensidade (Ω_λ) ($\lambda = 2, 4, 6$) e da taxa de emissão não-radiativa (A_{nrad}), não é possível projetar tais dispositivos de forma puramente teórica. Nossa grupo está buscando desenvolver modelos semiempíricos para os cálculos dos Ω_λ e A_{nrad} , a fim viabilizar o *design* teórico de sistemas contendo íons lantanídeos. A generalização dos modelos vem demandando bastante esforço.

METODOLOGIA

Nesse trabalho, apresentamos o protocolo para o *design*. Para tal, propusemos modificações nos ligantes de um sistema precursor (matriz). O escolhido foi o európio (III) tris-(4,4,4-trifluoro-1-fenil-1,3-butanodionato-O-O') – bis - (metanol). Como objetivo principal, buscarmos propor sistemas com rendimento quântico de emissão maior que o precursor. A Figura 1 apresenta o protocolo de *design*.

Figura 1: Protocolo para design teórico dos sistemas.



RESULTADOS

A Figura 2 apresenta o ligante tris-(4,4,4-trifluoro-1-fenil-1,3-butanodionato-O-O') – bis - (metanol). Na posição R1, adicionamos o grupo doador de elétrons NH₂ nos dirigentes orto, meta ou para. Em R2, acrescemos a cadeia fluorada em uma unidade (-CF₂), aumentando o tamanho do grupo aceptor de elétrons.

Figura 2: ligante tris-(4,4,4-trifluoro-1-fenil-1,3-butanodionato-O-O') – bis - (metanol).



A Tabela 1 apresenta os resultados das propriedades luminescentes experimentais do sistema precursor e resultados teórico dos sistemas propostos no processo de *design*.

Tabela 1: Propriedades luminescentes calculadas.

Sistema	Matriz	C_O	C_M	C_P
$\Omega_2 (x10^{-20})$	28,30	27,47	33,76	28,10
$\Omega_4 (x10^{-20})$	6,20	6,88	6,39	6,25
$\Omega_6 (x10^{-20})$	--	0,20	0,26	0,21
$A_{rad} (s^{-1})$	1019,49	997,93	1159,39	485,06
$A_{nrad} (s^{-1})$	596,02	642,19	485,06	632,45
$t (ms)$	0,6190	0,6172	0,6081	0,6174
$\eta (%)$	63,00	60,36	70,50	69,79
$q (%)$	60,00	59,75	69,79	60,25

Analisando a Tabela 1, é possível observar que o composto C_M apresentou A_{rad} , η e q superiores a todos os compostos, bem como A_{nrad} inferior aos mesmos.

CONCLUSÃO

Os modelos parametrizados para a determinação dos parâmetros de intensidade e Anrad permitiram que o estudo fosse realizado de forma independente dos dados experimentais. O objetivo do design foi realizado com sucesso, visto que o composto C_M possui q maior que o Matriz.

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Estrutura cristalina de alótropos do nitrogênio

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Palavras-Chave: estrutura cristalina, Teoria do Funcional da Densidade (DFT), molécula de nitrogênio, N₆

O nitrogênio é um elemento bastante comum e encontrado na natureza na forma N₂, correspondendo a cerca de 78% do ar na atmosfera terrestre. As moléculas de N₂ são altamente estáveis termodinamicamente, e outras estruturas contendo apenas átomos de nitrogênio (polinitrogênios) tendem a se dissociar liberando grande quantidade de energia [1]. Um ponto negativo dos materiais energéticos convencionais é a liberação de gases nocivos na combustão, e por esse motivo a busca por polinitrogênios tem despertado um grande interesse pelo potencial de produção de energia limpa e ecologicamente viável.

As ligações N-N de um polinitrogênio permitem obter vários tipos de estruturas complexas em relação ao tipo de arranjo, podendo ser subdividida nas subcategorias de: cadeia, anel ou gaiola de nitrogênio [2]. Nas últimas décadas, muitos trabalhos teóricos tem estudado a fase gasosa. Porém, a fase cristalina tem sido pouco explorada. Por isso, a motivação deste trabalho é buscar estruturas cristalinas mais adequadas para os polinitrogênios, além de prever suas estabilidades termodinâmica e cinética.

A metodologia empregada neste trabalho foi a Teoria do Funcional Densidade (DFT) como implementado no programa SIESTA [3]. Empregamos pseudopotenciais de norma conservada gerados segundo o esquema de Troullier-Martins [4] na forma fatorada de Kleinman-Bylander [5]. Na simulação da estrutura cristalinas do N₆, utilizou-se um grid no espaço real equivalente a uma energia de 350 Ry. Para o funcional de troca e correlação utilizou-se dois funcionais: GGA/PBE e o vdW/DRSLL [6-7].

É sabido que a forma prismane do N₆ possui um barreira de dissociação alta e pode ser estável em uma forma cristalina [1,8]. Com o objetivo de descrever quais fases cristalinas são mais adequadas para essa molécula, realizamos uma varredura em estruturas conhecidas na literatura. Inicialmente testamos 4 fases cristalinas conhecidas: cúbica simples (sc), cúbica de face centrada (fcc), cúbica de corpo centrado (bcc) e hexagonal compacta (hcp). Para essas fases, construímos curvas de equação de estado E (V) e determinamos a energia E₀ mínima de cada fase cristalina, bem como os parâmetros de rede ótimos. A partir de cada mínimo da curva E(V) fizemos uma relaxação completa das posições e da rede e determinamos a rede cristalina mais estável para o

N₆. Os resultados mostram que uma estrutura triclinica é a fase mais estável com parâmetros cristalográficos: a = 4,48 Å, b = a, c = 4,72 Å, α = 110,44°, β = 69,31°, γ = 71,75°.

Como perspectiva futura, estudaremos as fases cristalinas de outras moléculas de nitrogênio do tipo N₈ e N₁₀. Para esses casos, pretendemos utilizar um algoritmo para predição de estruturas cristalinas como o USPEX (Universal Structure Predictor: Evolutionary Xtallography) [9].

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First-principles study of lanthanide-based inorganic-organic hybrid system for photon upconversion

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keywords: *dft, cyanine, tddft*

Solar energy is the most promising renewable energy source, and therefore, solar cell power conversion efficiency (PCE) is a primary concern. The theoretical maximum conversion efficiency for solar cells is known as the Shockley-Queisser limit, and to go beyond it is crucial to improve the PCE. One approach to surpass this limit is by upconversion and the strategy consists of attaching an antenna to a nanoparticle doped with lanthanides [1]. The antenna will absorb near infrared light, transfer the excitation to the nanoparticle that ultimately will perform the upconversion. The aim of this study is to investigate the photophysical properties of a cyanine dye analogue to be used as antenna, performing first-principles calculations based on Density Functional Theory (DFT) [2,3] and Time Dependent-DFT [4].

The calculations were performed to obtain geometry, absorption, emission and difference density plots, in gas phase and considering solvation effects implicitly and explicitly. Different exchange-correlation (XC) functionals were considered, such as hybrids, GGA, meta hybrids and range separated hybrids. The calculations were performed using Amsterdam Density Functional (ADF) [5].

The absorption showed a trend regarding different exchange-correlation (XC) functionals, with maximum near 865 nm for hybrids, 926 nm for GGA and 1484 nm for a meta hybrid. Moreover, the molecule presented a Stokes Shift of 157 nm for B3LYP and bathochromic shifts related with the solvent's polarity. A vinylene shift study were also performed using different functionals, in order to understand the trend of the maximum absorption for different lengths of the polymethine chain, as well as different substituents that can be used as linkers to attach to the nanoparticle.

These results are an important qualitative characterization in agreement with previous studies regarding the DFT limitations to describe cyanine dyes using hybrid and GGA functionals, and the better agreement when using meta hybrid M06-HF.

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Theoretical Investigation of the Reaction Mechanism Between Dopamine and S-citronellal catalyzed by the Norcoclaurine Synthase (NCS)

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Keywords: *Norcoclaurine Synthase, Reaction Mechanism, Quantum Chemical Calculations.*

Introduction

The Pictet Spengler (PS) reaction is characterized by the condensation of a β -phenylethylamine and an aldehyde or ketone to produce tetrahydroisoquinoline alkaloids (THIQ). In nature, the PSases are the enzymes responsible for the PS reaction leading to important THIQ derivatives such as morphine and noscapine. The Norcoclaurine Synthase (NCS) is a PSase involved in the condensation between dopamine and 4-hydroxyphenylacetaldehyde (4-HPAA) to produce the s-norcoclaurine, the first metabolite in the biosynthesis pathway of such alkaloids.

The NCS has demonstrated great promiscuity towards aldehydes and ketones. In order to rationalize the NCS mechanism of action, some propositions on the substrates binding mode and reaction mechanism were made. Since then, structural evidences supported by quantum calculations were presented shedding light onto this matter, and indicating a mechanism for the formation of the s-norcoclaurine. However, the mechanistic pathway involved in the enzymatic PS reaction is still under investigation. In this sense, in this work we investigate the enzymatic PS reaction mechanism for the condensation between the dopamine and the s-citronellal, which has been experimentally tested and reported to be active for the NCS.

Methodology

In this work, we used the cluster approach, which consists of using quantum chemical methods to treat a chosen part of the enzyme around the active site, while the rest of the enzyme is approximated as a homogeneous medium.

In this sense, our cluster model consists of 23 amino acids (Y63, S64, W65, P66, G67, L68, A69, L72, L76, L95, M97, F99, Y108, Q110, F112, K122, V124, M126, Y139, D141, T159, L180, and M183, from PDB ID 5NON) truncated at the α -carbon, three water molecules, and the substrates dopaminium and s-citronellal.

All steps of the mechanism were investigated using DFT. The geometry optimizations and vibrational frequencies at 1 atm and 298.15 K were performed at the PBE-D3(BJ)/SV(P) level of theory, using RI approximations and def2/J auxiliary basis set. Single-point energies were performed at B3LYP-D3(BJ)/def2-TZVP(-F) level of theory, using RIJCOSX and def2/J. The TS calculations were performed using the Nudged Elastic Band (NEB) method.

Results and Discussion

The proposed mechanism for the enzymatic-catalyzed condensation between dopaminium and s-citronellal in this work is shown in Figure 1.

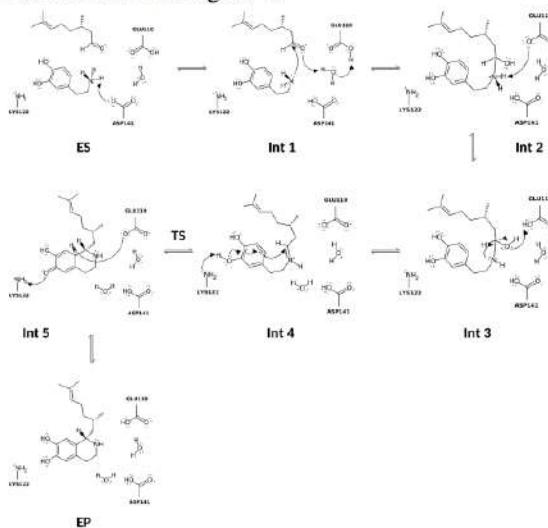


Figure 1. This work proposed reaction mechanism.

This mechanism features three less intermediates in the overall reaction compared to the proposed mechanism for the 4-HPAA substrate. Also, we show that the substrate flexibility plays an crucial role in the reaction, accounting for part of the energy barrier at the cyclization step. This agrees with experimental data showing that the variant L76A increases the K_{cat} of the NCS for the s-citronellal. In our calculations, we observed the aliphatic portion of the forming molecule constrained by the residue L76. Furthermore, we also demonstrate that water molecules in the active site create a net of hydrogen-bonds bridging the amino acids, helping the stabilization of charges and intermediates featuring a loss of aromaticity.

Conclusion

We demonstrate a reduced reaction mechanism accounting for all important PS reaction steps. Also, we showed that the aldehyde-scope accepted by the NCS might be related to substrate flexibility.

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Determinação das constantes de velocidade dos mecanismos de formação do ozônio troposférico a partir de reações fotoquímicas envolvendo o acetaldeído como precursor

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Palavras-Chave: smog-fotoquímico, cinética, redes neurais artificiais.

Introdução: A alta concentração de ozônio na troposfera é um grave problema ambiental. A produção desta molécula em nível troposférico está relacionada com a emissão de gases poluentes em grandes centros industriais. Entre estes gases destacam-se os óxidos de nitrogênio (NO_x), os compostos orgânicos voláteis (COVs) e compostos de enxofre, que quando submetidos à radiação solar se tornam um sistema poluente gerador de moléculas de ozônio, formando o fenômeno conhecido como *smog-fotoquímico* [1,2]. Muitos mecanismos que levam à formação do ozônio são bem fundamentados na literatura, no entanto, suas constantes de velocidade são difíceis de serem determinadas experimentalmente por se tratarem de reações fotoquímicas.

Objetivo: Este trabalho teve como objetivo promover um estudo cinético das reações fotoquímicas de formação da molécula de ozônio a partir da degradação do acetaldeído em condições troposféricas.

Metodologia: A cinética envolve um mecanismo constituído de cinco etapas, e as constantes de velocidade para as quatro últimas etapas foram obtidas a partir de dados experimentais da primeira delas [3]. A constante de velocidade de cada etapa da reação foi determinada de forma teórica por meio de uma abordagem fundamentada na perspectiva do problema inverso da cinética química, utilizando-se um método numérico baseado em redes neurais artificiais (RNA) do tipo Hopfield [4], e, também aplicando-se o algoritmo Levenberg-Marquardt, frequentemente utilizado em problemas similares.

Resultados: os valores obtidos e a constante experimental utilizada constam na tabela abaixo:

Tabela: Constantes de velocidade das etapas de consumo do acetaldeído na troposfera

Etapas	Constantes (k) ($\text{cm}^3 \cdot \text{molécula}^{-1} \cdot \text{s}^{-1}$)	
	Algoritmo RNA	Levenberg-Marquardt
1º	$*1,50 \cdot 10^{-11}$	$*1,50 \cdot 10^{-11}$
2º	$1,09 \cdot 10^{-12}$	$1,09 \cdot 10^{-12}$
3º	$7,52 \cdot 10^{-14}$	$7,53 \cdot 10^{-14}$
4º	$4,72 \cdot 10^{-15}$	$4,53 \cdot 10^{-15}$
5º	$6,52 \cdot 10^{-16}$	$6,72 \cdot 10^{-16}$

*constante experimental.

Os valores encontrados apresentam um erro médio para a reprodução dos dados experimentais de, no máximo, 7,03%, e uma energia de rede (diferença entre a norma euclidiana dos vetores com os dados teóricos e experimentais) entre 0,00720 a 0,02356, indicando um bom ajuste do modelo. Além disso, a semelhança numérica entre os valores determinados por ambos algoritmos indica uma significativa precisão dos dois algoritmos para a resolução do problema.

Relacionando as constantes encontradas com a Teoria do Estado de Transição, foi possível determinar os valores de *energia livre de Gibbs de ativação* das cinco etapas: 134,75; 141,22; 147,86; 154,72 e 159,62, respectivamente, a temperatura de 298K e com unidade medida igual $\text{kJ} \cdot \text{mol}^{-1}$.

Conclusão: Foi possível observar como a utilização de redes neurais artificiais do tipo Hopfield é uma eficiente estratégia para determinação de problemas inversos mal-colocados em química como o apresentado pelo caso do *smog-fotoquímico*.

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Theoretical study of a new system of Eu(III) Pyromellitic of Intense Red-Orange Luminescence and High Thermal Stability for Marking in Gunshot Residues

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Palavras-Chave: Európio, Luminescência, GSR.

INTRODUCTION

Systems containing Eu³⁺ ions have been extensively studied due to their wide range of applications as luminescent devices¹. Thus, in this work we studied the spectroscopic properties of a trivalent europium complex isolated from a metal-organic framework – MOF, [EuHbtac]_n, supported by 1,2,4,5-benzenetetracarboxylic acid (pyromellitic acid).

METHODOLOGY

Initially, the optimization of the MOF geometry was performed using the semiempirical Sparkle/RM1² model in program MOPAC³. Subsequently, the calculations of the singlet and triplet excited state energies were made using the INDO/S-CIS⁴ method, which is implemented in the ORCA⁵ program. Then, the entire theoretical study was carried out using only the LUMPAC⁶ software, because it is implemented all the models described below. The intensity parameters were calculated using the QDC⁷ Unicity model that makes use of the Judd-Ofelt^{8,9} theory. Finally, energy transfer and back-transfer rates are calculated., Eu³⁺ - binding atom, which were determined through the model developed by Malta¹⁰. From these rates and the radiative and non-radiative decay rates, it was possible to calculate the quantum efficiency and the quantum yield for each of the systems.

RESULTS AND DISCUSSION

The theoretical and experimental values for the radiative and nonradiative emission rates (A_{rad} and A_{nrad} , respectively), intensity parameters (Ω_2 , Ω_4 , and Ω_6), quantum efficiency (η), and quantum yield (q) for [EuHbtac]_n are summarized in Table 1.

Upon analyzing the data it is clear that the theoretical and experimental values are in excellent agreement. In addition, it was possible to highlight that the high value for the experimental Ω_2 parameter is closely related to the character of hypersensitivity of the $^5D_0 \rightarrow ^7F_2$ transition.

The main energy transfer channels (with higher energy transfer rates) were $T_1 \rightarrow ^5D_1$ and $T_1 \rightarrow ^5D_0$.

Table 1: Theoretical and experimental spectroscopic parameters.

	Exp	Sparkle/RM1
$\Omega_2 (10^{-20} \text{ cm}^2)$	5.73	5.73
$\Omega_4 (10^{-20} \text{ cm}^2)$	5.25	5.24
$\Omega_6 (10^{-20} \text{ cm}^2)$	---	0.0835
$A_{rad} (\text{s}^{-1})$	299.56	300.75
$A_{nrad} (\text{s}^{-1})$	520.10	518.93
$\eta (%)$	36.55	36.69
$q (%)$	---	36.32

The A_{nrad} values are greater than the A_{rad} values, which may be caused by the network vibration (energy dissipation through phonons) and by the presence of the O-H oscillators, once one of the carboxylate groups is protonated. Due to its intense emission and high thermal stability (it is a MOF), the system was utilized for marking of gunshot residues (GSRs), with its preliminary tests showing very promising results.

CONCLUSION

The photophysical study shows an efficient antenna effect, which resulted in a good quantum yield with intense emission in the red region. This provided application in the area of public security working as a good marker of ammunition.

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Probing Toxin Membrane Interactions with Enhanced Sampling Method

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Keywords: mycolactone, metadynamics, membrane.

INTRODUCTION Mycolactone is a cytotoxic and immunosuppressive macrolide produced by *Mycobacterium ulcerans* and is the sole causative agent of the neglected tropical skin disease Buruli ulcer. The disease is characterized by necrotic lesions that lack pain and wound healing, which can lead to permanent disfigurement and disability if left untreated. The toxin invades and kills host cells primarily through a range of interactions, including uncontrolled actin branching and blocking the sec61 translocon.^{1,2} As a small amphiphilic molecule, mycolactone traverses the host system by associating with lipophilic carriers, including membranes. It diffuses from the Plasma Membrane (PM) to the Endoplasmic Reticulum (ER) in 1-2 minutes.² Thus, understanding how the toxin is distributed in and navigates the host system via membranes and other lipophilic structures is essential to developing effective diagnostic assays. In this work, we applied all-atom molecular dynamics simulations with an enhanced sampling method to comprehend how the toxin interacts with different lipophilic architectures and understand how it invades and navigates the host environment.

METHODOLOGY The complexity of membranes is staggeringly challenging to capture in simulations. But modeling realistic membranes is essential for specificity. So, we built models with different phospholipid compositions: ER (POPC, POPE) and PM (DPPC, POPC, POPE, and Cholesterol). Simulation of membrane permeation often requires enhanced free-energy sampling. For this work, we used Transition-Tempered Metadynamics.³ To capture the process of permeation, we defined as the collective variables (CVs): the center of mass of the lactone ring (translation), and the angle between the vector connecting the hydroxyl groups on the end of the northern and southern tails and the vector normal to the lipid bilayer (orientation). We have run seven replicas of each membrane system for 5 μ s. The membranes were modeled using an Amber-based force field with corrections to balance the hydrophilic and hydrophobic forces. Water molecules used the TIP3P force field.

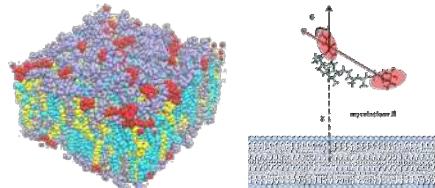


Fig. 1. Representation of PM membrane and the CVs.

RESULTS The average of the Minimum Free Energy Path (MFES) for each membrane shows that we were able to find the basin points and the path that connects. More extended simulations were required in our studies as the permeability coefficient got more accurate with better convergence.

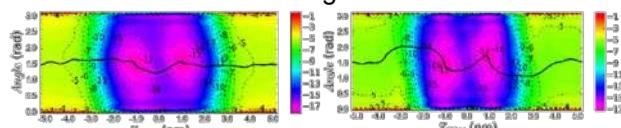


Fig. 2. MFES for the ER (left) and PM (right).

The average paths were similar between the membranes, and there were minor differences among the replicas. PM has a slightly better separation between the deeps. The lowest energy in the MFEP for both membranes shows a C-shaped arrangement for the toxin. The Lactone ring interacts with the hydrophobic chains, while the Northern and Southern chains (hydrophilic) point to the lipid head groups.

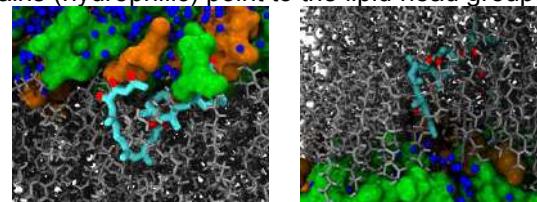


Fig. 3. Lowest energy cluster for the ER (left) and PM (right).

To study the water role in the permeation path, we calculated the probability and the position distribution of the number of water molecules interacting with the toxin through the simulation. More water molecules were detected in the inner parts of the ER bilayer than in the PM. Thus, decreasing the energetic barrier of the chains permeating in the hydrophobic core.

CONCLUSIONS Our results show a strong association of the toxin with membranes, especially the ER. Membrane composition influences the association of the toxin with the membrane. Cholesterol makes PM more rigid, increasing the height and width of the energy barrier. Water molecules play an important role in the amphiphile permeation.

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Estudo teórico das reatividades de potenciais fármacos COVID-19

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Palavras-Chave: SARS-CoV-2, Índices de Fukui, Cálculos de estrutura eletrônica.

Introdução

SARS-CoV-2, também conhecido como novo coronavírus, foi identificado em Wuhan na China no final do ano de 2019. Tal vetor viral é responsável pela COVID-19, doença altamente contagiosa que causou uma pandemia em 2020 e que ainda perdura em 2021. Milhões de pessoas foram a óbito, além disto, a economia dos países foram afetadas com prejuízos financeiros significativos.

Apesar de atualmente existirem vacinas para combater o vírus, ainda assim uma grande parcela da população não foi vacinada. Neste contexto, é grande a necessidade de que medicamentos eficazes sejam desenvolvidos para auxiliarem na profilaxia dessa moléstia¹.

Este trabalho tem por objetivo propor um mecanismo de estudo ao avaliar as reatividades de potenciais fármacos. Pelo fato do novo coronavírus ser um retrovírus, analisar também as reatividades das bases nitrogenadas constituintes do RNA e como elas se relacionam com os medicamentos alvos.

Metodologia

Os materiais avaliados no presente estudo foram os fármacos remdesivir e favipiravir² e também as bases nitrogenadas constituintes do RNA: adenina, citosina, guanina e uracila. Ensaios *in vitro* têm demonstrado a potencialidade destas drogas.

As geometrias dos compostos foram otimizadas numa abordagem DFT/B3LYP/6-31G(d). O estudo da reatividade foi realizado por meio da análise dos Índices de Fukui Condensados sobre os átomos (IFCA)³ e maciez química global. Os cálculos foram realizados com o auxílio do pacote computacional Gaussian 09⁴.

Resultados

A Figura 1 mostra os resultados dos cálculos de IFCA para os diferentes fármacos e bases. Cores azul e vermelho denotam, respectivamente, regiões de menor e maior reatividade. As demais colorações indicam reatividades intermediárias seguindo uma escala RGB (red-green-blue). A figura 2 apresenta a maciez química global dos compostos. De forma geral, nota-se que o favipiravir possui a reatividade na cadeia principal e o remdesivir na extremidade. As bases nitrogenadas possuem a reatividade nos anéis aromáticos e não nos açúcares e grupos fosfato.

Analizando a figura 2, nota-se que a maciez química global dos fármacos e das bases são bem próximas, mostrando que há uma boa interação entre eles.

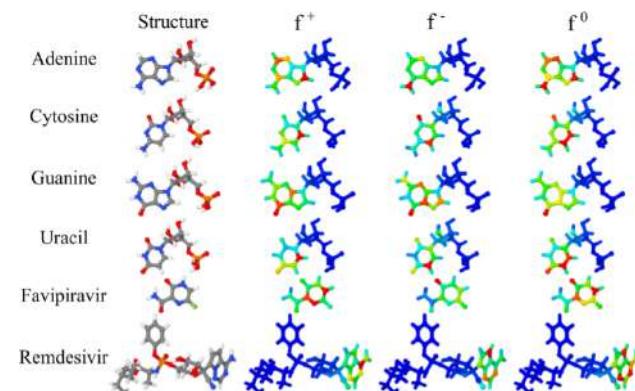


Figura 1. IFCA dos medicamentos e bases. f^+ , f e f^0 significam índices para agentes nucleofílicos, eletrofílicos e radicalares.

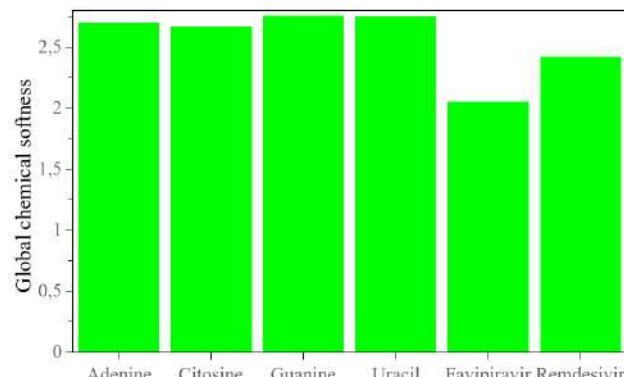


Figura 2. Maciez química global dos compostos.

Conclusões

O presente trabalho mostra a importância do estudo das reatividades de potenciais medicamentos e das bases constituintes do material genético do SARS-CoV-2. Através da análise da maciez química global, é possível averiguar uma forte interação entre os fármacos e as bases. Com isto, é possível auxiliar estudos experimentais para desenvolver e/ou descobrir remédios para o tratamento desta doença.

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Agradecimentos

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Aplicação de Métodos Computacionais no Estudo do Mecanismo de Ação de Enzimas Essenciais ao Vírus Zika

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Palavras-Chave: vírus zika, QM/MM, dinâmica molecular

Introdução

O vírus Zika (ZIKV) é um vírus essencialmente transmitido por artrópodes, principalmente por mosquitos do gênero *Aedes* (*Ae. aegypti*, *Ae. africanus*, *Ae. hensilli*, e *Ae. albopictus*)¹.

Os dados epidemiológicos revelaram que este vírus, tido como relativamente inofensivo, agora está associado a distúrbios patológicos graves incluindo microcefalia em recém-nascidos e síndrome de Guillain-Barre em adultos².

Esforços recentes têm revelado uma série de proteínas essenciais ao ciclo de vida do vírus Zika, e que podem ser usadas como alvo na busca de novos medicamentos.

O processo de replicação viral, em que a poliproteína precursora libera as proteínas para a formação do vírus é mediada por co- e pós-tradução de proteases do hospedeiro e por dois componentes da própria protease do vírus, o domínio protease da NS3 (NS3pro) e a NS2B, que funciona como cofator. A NS3pro é, como a tripsina, uma protease de serina, contendo uma tríade catalítica composta pelos resíduos His, Asp e Ser. A proposta desse trabalho é a compreensão detalhada do mecanismo e a identificação das espécies intermediárias na reação catalisada pela protease de serina ZIKV.

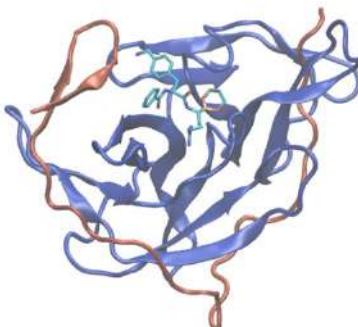


Figura 1: Estrutura cristalina, PDB-ID:5LC0, do monômero NS2B-NS3 protease com inibidor (C25H35BN6O5)ZIKV. O cofator NS2B (vermelho) e a NS3 protease (azul).

Metodologia

Utilizamos dinâmica molecular com método híbrido QM/MM³ e com método de amostragem Umbrella Sampling⁴ para calcular as mudanças de energia livre associadas com os dois passos químicos da reação. Na primeira etapa, a ligação peptídica é clivada através de um ataque nucleofílico do grupo hidroxila da serina (Ser) ao carbono do

grupo carbonila (substrato), formando um intermediário tetraédrico acil-enzima, que é desfeito quando a ligação peptídica é quebrada (Figura 2). A etapa limitante para a velocidade da reação é o processo de acilação, cuja velocidade é determinada pela formação do intermediário tetraédrico estável

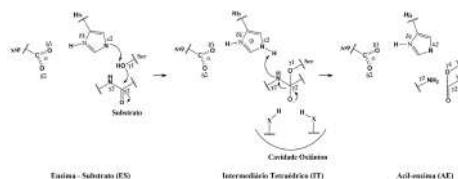


Figura 2: Ilustração do mecanismo de reação da NS2B-NS3 protease com o substrato para a quebra da ligação peptídica.

Resultados:

A linha tracejada da Figura 3 mostra que a NS2NS3 protease do vírus Zika apresenta uma primeira etapa concertada em que a transferência do próton (d1) e o ataque nucleofílico (d2) acontecem ao mesmo tempo. A barreira para a formação desse estado intermediário tetraédrico (TI), é de 33,62 kcal/mol.

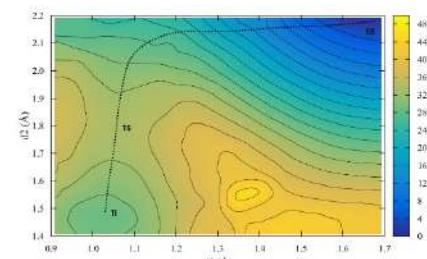


Figura 3: Perfil de energia livre tridimensional (ou PMF) QM(PM3PDDG)/MM para a formação do intermediário tetraédrico (TI) pela reação da NS2B-NS3 protease com o substrato (VLLR).

Conclusão:

Obtivemos o perfil energético para a primeira etapa da reação, formação do intermediário tetraédrico com energia livre de 33,62 kcal/mol. Outras particularidades serão mostrados no evento.

Agradecimento

Ao suporte financeiro da Fundação de Amparo a Ciéncia e Tecnologia do Estado de Pernambuco (FACEPE).

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Avaliação do método SCC-DFTB em clusters para a simulação de líquidos iônicos

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Palavras-Chave: DFTB, DFT, Ionic Liquids.

Introdução

Por apresentarem uma boa janela eletroquímica, alta condutividade iônica e baixo impacto ambiental, líquidos iônicos (LIs) possuem um grande potencial para serem aplicados como eletrólitos em sistemas eletroquímicos para armazenamento de energia, como em supercapacitores a base de grafeno.¹ Afim de se realizar a modelagem em tamanho adequado do líquido e da interface com grafeno, a metodologia semiempírica SCC-DFTB (*self-consistent charge density functional tight binding*) é bastante promissora por apresentar acurácia comparada à métodos DFT, mas com tempo de convergência de 100 a 1000 vezes menor.² LIs a base de 1-alquil-3-metilimidazólio e tricianometanida, $[C_nC_1im][C(CN)_3]$, apresentam nanoestruturação devido à competição entre as interações eletroestáticas de longo alcance provenientes dos grupos carregados e as interações hidrofóbicas de curto alcance das cadeias alquilas do cátion³. A fim de se obter uma descrição adequada das propriedades desse sistema, portanto, é necessário garantir que a metodologia utilizada reproduza corretamente as interações intra- e intermoleculares no líquido.

Metodologia

Foi avaliada a performance do método SCC-DFTB com os conjuntos de parâmetros mio-1-1 e 3ob-3-1 (frequências: 3ob:freq-1-2) para a obtenção da energia de formação,⁴ de parâmetros estruturais e dos modos vibracionais partindo da otimização de geometria de pequenos clusters de $[C_2C_1im][C(CN)_3]$ frente a métodos DFT de referência baseados em resultados da literatura:⁵ PBE-D3/cc-PVTZ, BLYP-D3/cc-PVTZ e ω B97XD/aug-cc-PVDZ. Analisou-se as frequências em relação ao espectro de reflexão total atenuada no infravermelho com transformada de Fourier (ATR-FTIR) do líquido. Nos cálculos em DFTB foi utilizado correção de dispersão DFT-D3 com BJ-damping e correção para o hidrogênio. Softwares utilizados: DFTB+,² e Gaussian09.⁶

Resultados

O diedro ϕ do cátion (Figura 1) mostra que há uma tendência de formação de clusters com a cadeia lateral do imidazólio sobre o ânion pelos métodos DFTB. Em DFT, há a formação de estruturas com a

cadeia aproximadamente paralela ao anel (Tabela 1). A melhor reprodução da banda experimental em 959.1 cm⁻¹ pelo modo v das estruturas com cadeias em paralelo indica preferência dessas no líquido.



Figura 1 Estrutura otimizada de um cluster de $[C_2C_1im][C(CN)_3]$. O diedro ϕ é definido pelos átomos C1-N2-C4-C5. O deslocamento dos átomos no modo v é representado pelos vetores. (Avogadro)⁷

Tabela 1 Erro médio (MSE) e desvio padrão médio (RMSD) na energia de formação e diedro ϕ do imidazólio frente ao método PBE-D3/cc-PVTZ. Posição do modo v frente à banda em 959.1 cm⁻¹ do espectro ATR-FTIR experimental. Tempo de CPU médio (TM) para o cálculo de otimização de geometria por método.

	$E_{form}/\text{kJ mol}^{-1}$		ϕ/graus		ν/cm^{-1}		TM
	MSE	RMSD	MSE	RMSD	MSE	RMSD	
SCC-DFTB/ <i>3ob</i>	3,8	0,6	76,0	139,1	43,9	12,0	00:00:07:50
SCC-DFTB/ <i>mio</i>	-3,7	1,2	67,2	110,9	92,2	5,4	00:00:03:35
BLYP-D3/cc-PVTZ	6,1	0,3	-6,1	2,2	-16,5	4,8	20:08:11:40
ω B97XD/aug-cc-PVDZ	4,5	0,3	-0,1	2,3	-13,1*	0,6	22:21:53:04
PBE-D3/cc-PVTZ					-12,0	6,0	20:00:28:40

*fator de escala: 0,957 (NIST).

Conclusões

Apesar da reprodução das energias de formação, os conjuntos de parâmetros mio-1-1 e 3ob-3-1 não se mostraram eficazes em reproduzir as interações intermoleculares e as estruturas dos clusters de $[C_2C_1im][C(CN)_3]$, com uma maior interação da etila do cátion com o ânion. Novos parâmetros serão propostos para a elaboração de um modelo que permita a simulação correta da fase *bulk* do líquido e em sistemas confinados por superfícies de grafeno.

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THEORETICAL STUDY OF THE PHOTOLUMINESCENT PROPERTIES OF THREE EU(III) HYDROCINNAMATES CONTAINING DIFFERENT AUXILIARY LIGANDS

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Keywords: LUMINESCENCE, LUMPAC, INTENSITY PARAMETERS.

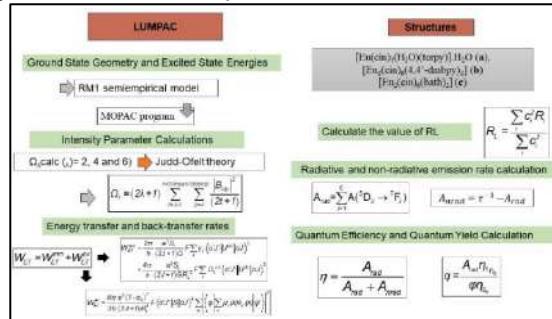
INTRODUCTION

In light-emitting materials, 4f-4f transitions are responsible for interesting photophysical properties. Trivalent lanthanide ions, Eu³⁺ with the main emitter level ⁵D₀ and ground state ⁷F₀ is one of the most studied, forming very stable luminescent compounds with ligands containing oxygen and nitrogen donor atoms [9]. In this context, aromatic carboxylates such as Hcin, in addition to having a high complexing power, also act as efficient sensitizers of the Eu³⁺ ion, presenting excellent results as Molecular Light Conversion Devices (LCMDs)[1]. This work proposes the investigation of the energy transfer process, for the three Eu³⁺ complexes, containing the 2.2' auxiliary ligands: (terpy), (4,4'-dmbpy) and (bath), and the role of auxiliary binders in the emission process. For this, the various spectroscopic properties, such as: energy transfer (W_{ET}), back transfer (W_{BT}), radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates, intensity parameters Ω_λ ($\lambda = 2, 4$ and 6), Quantum efficiency (η) and quantum yield (q) of Eu³⁺.

METHODOLOGY

The calculation of spectroscopic properties followed the protocol defined in LUMPAC software as shown (Figure 1).

Figure 1. Theoretical protocol used.



RESULTS

Through the RM1 model, the optimized ground state geometries were obtained (Figure 2), and posteriorly used in the energy transfer process elucidation. The results obtained for the spectroscopic properties for the hydrocinnamate Eu³⁺ are shown in Table 1. The theoretical values were in excellent agreement with the experimental, corroborating the structural proposals.

Figure 2: Geometry optimized for the three complexes

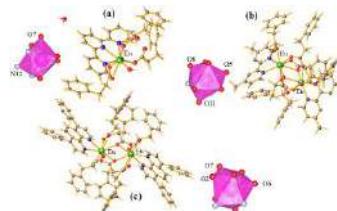


Table 1: Spectroscopic properties of Eu³⁺ hydrocinnamates

	Ω ₂ (cm ⁻¹)	Ω ₆ (cm ⁻¹)	A _{rad} (s ⁻¹)	Ω ₁ (cm ⁻¹)	Ω ₂ (cm ⁻¹)	A _{rad} (s ⁻¹)	Ω ₁ (cm ⁻¹)	Ω ₂ (cm ⁻¹)	A _{rad} (s ⁻¹)	Ω ₁ (cm ⁻¹)	Ω ₂ (cm ⁻¹)	A _{rad} (s ⁻¹)
1	5.20	7.04	8.115	319.25	1014.05	23.95	23.15			5.20 × 10 ⁻³	7.04 × 10 ⁻³	7.04 × 10 ⁻³
	5.20	7.04	312.19	1021.14	23.41					T ₁ → ⁵ D ₁ 4.32 × 10 ³	T ₁ → ⁵ D ₁ 1.0 ³	T ₁ → ⁵ D ₁ 1.0 ³
2	6.28	7.10	11.045	251.75	171.81	67.18	64.00			T ₁ → ⁵ D ₁ 1.02 × 10 ³	T ₁ → ⁵ D ₁ 0.91 × 10 ³	T ₁ → ⁵ D ₁ 0.91 × 10 ³
	6.28	7.11	345.01	177.95	66.61					T ₁ → ⁵ D ₁ 3.11 × 10 ³	T ₁ → ⁵ D ₁ 0.82 × 10 ³	T ₁ → ⁵ D ₁ 0.82 × 10 ³
3	8.08	8.32	8.158	440.08	168.88	22.30	71.28			S→ ⁵ D ₁ 7.78 × 10 ³	S→ ⁵ D ₁ 1.38 × 10 ³	S→ ⁵ D ₁ 1.38 × 10 ³
	8.08	8.32	439.75	168.98	22.12					T ₁ → ⁵ D ₁ 3.82 × 10 ³	T ₁ → ⁵ D ₁ 1.03 × 10 ³	T ₁ → ⁵ D ₁ 1.03 × 10 ³

The highest energy transfer rates are found in compound **1**, but the quantum efficiency of this complex is low, due to the presence of the coordinating water molecule. Observing compounds **2** and **3**, the rates T₁→⁵D₁ and T₁→⁵D₀, the **3** has values two orders of magnitude higher for the back transfer rates ⁵D₁→T₁ and ⁵D₀→T₁, justifying the higher quantum efficiency value observed in this complex.

CONCLUSIONS

The photoluminescent properties showed that the values of the ⁵D₀→⁷F₀ transitions and Ω₂ are reflected in the coordination mode of the carboxylate groups to the Eu³⁺ ions. Thus the structure/photoluminescence relationship may open the possibility of developing new spectroscopic sensors based on Eu³⁺ coordination compounds.

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Experimental and computational study of the energy transfer pathways of Eu^(III) isothiocyanate compounds

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Keywords: LMCT, Lanthanides, TDDFT.

Introduction

Comprehension of the energy transfer mechanisms is a paramount step to explain the luminescence exhibited and to design even more efficient lanthanide compounds, once that the efficiency of such processes is dependent on the energy levels structure, as well the non-radiative process like multi-phonon decay and low lying ligand-to-metal charge transfer (**LMCT**) states. This last process is applied to explain the low luminescent properties of Eu^(III) complex, if the multi-phonon deleterious pathway is discard[ref]. In order to achieve an insight on the energy transfer mechanism and the luminescence quenching *via LMCT* that is observed for the [Eu(NCS)₃(na2ap)₂]²⁺.2H₂O (with na2ap = N-(pyridin-2-yl)acetamide) compound, a mixed experimental/theoretical investigation was performed.

Methodology

Diffuse reflectance and UV-visible absorption spectra were acquired for [Ln(NCS)₃(na2ap)₂]²⁺.2H₂O (LnNA2AP) and [TBA]₃[Ln(NCS)₆] (LnTBA) compounds (Ln = Gd and Eu, TBA = Tetrabutylammonium). Triplet energy was obtained from GdNA2AP phosphorescence spectra. Geometry optimization, frequency and TDDFT calculations of EuNA2AP were performed with ORCA 4.2.1¹, Eu^(III) being treated by large core **46-f⁶RECP** and its associated valence basis, triple zeta quality **def2-TZVP** basis set was applied for the remaining atoms, **B3LYP** functional was adopted[ref]. For EuTBA, all electrons TDDFT calculation with **ZORA** Hamiltonian was performed, CAM-B3LYP functional, SARC2-ZORA-QZVP basis set for Eu^(III) and ZORA-def2-TZVP basis set for all other atoms were used.

Results and discussion

Comparison of the diffuse reflectance spectra of Gd^(III) and Eu^(III) analogous compounds indicated the presence of an additional absorption on the Eu^(III) counterparts which was addressed to the absorption of a LMCT state with an experimental energy almost invariant for the two Eu^(III) compounds (EuNA2AP

and EuTBA) and being located at 22624 cm⁻¹, this is slightly above of the ⁵D₀ and ⁵D₁ levels of the Eu^(III) (17293 cm⁻¹ and 19027 cm⁻¹, respectively) and below the first triplet of GdNA2AP compound (**T** experimental energy is 25188 cm⁻¹). Predicted TDDFT energies of the 4 initial **T_n** states (25357, 25806, 26094 and 26461 cm⁻¹) are in good agreement with experimental value of **T** and a closer look to the composition of these **T_n** states shows that the main single excitations are essentially HOMO/HOMO-1 ('NCS centered) and LUMO/LUMO+1 (centered on the **na2ap** moieties) transitions. Furthermore, TDDFT calculations on EuTBA indicates that the **LMCT** state (24690 cm⁻¹) is below the energies of experimental and theoretically determined **T** states. TDDFT spectra of EuNA2AP matches quite well the one recorded on ethanol for the [Eu(NCS)₃(na2ap)₂]²⁺.2H₂O compound and the analysis of the singlet states shows that the most intense absorption bands are predominantly composed by single excitations with π→π* character and are centered on the **na2ap** moieties.

Conclusions

Experimental and TDDFT calculations are in good agreement for the values of **T** state in EuNA2AP compound. **LMCT** energy resulting from relativistic TDDFT calculation on EuTBA indicates that this **LMCT** state is energetically closer and lies below the **T** state of EuNA2AP, which in turn is the responsible for populating the emissive levels of the Eu^(III)². This configuration of **T** and **LMCT** states suggests that the luminescence quenching observed on EuNA2AP compound is a consequence of the excitation energy being transferred from **T** to **LMCT**, which is a dramatically efficient way for quenching Eu^(III) luminescence³.

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Ab initio study of graphenylene-like nanostructures of silicene, germanene and siligene

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Palavras-Chave: 2D materials, porous nanostructures, graphenylene-like.

Since graphene was experimentally obtained, the search for other layered bidimensional (2D) materials has grown significantly, and graphene-like nanostructures such as silicene and germanene have been studied computationally and experimentally. Within the layered materials, porous nanostructures are an interesting type of material since they can have many applications beyond the graphene-like materials. There are studies showing the possibility to use them as lithium-ion battery anodes, as energy store medium, as well as catalyst materials. One example of a porous material is the graphenylene.

Graphenylene (GP) is a 2D carbon allotrope formed by two hexagonal rings connected via a tetragonal ring (biphenylene network). The GP has been theoretically studied for some years. Calculations shown that, different from graphene, the graphenylene layer present a small direct band gap around 25 meV [1]. Besides the layer, GP is also studied in the nanotube form and present a band gap dependent of the size and the chirality of the nanotube [2]. And recently the GP was experimentally obtained by Qitang and collaborators [3] opening a new class of 2D materials to be used in different applications.

Given the advancements in the synthesis of nanomaterials, it is likely that graphenylene-like structures will be grown in the near future. With this in mind, in this work we study the electronic and structural properties of silicene, germanene and siligene in the graphenylene-like structure within the density functional theory (DFT) framework as implemented in the SIESTA code. From the band structure analysis we can observe that homogeneous Si and Ge present a metallic character while the heterogeneous compound (SiGe) is semiconductor.

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**Assessment of electronic structure methods for the calculation of complexes between amino-acids and copper ions: application to copper bisglycinate and the GHK peptide****André Luís Pesquero de Melo, Maurício Domingues Coutinho Neto**

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Palavras-Chave: peptídeos, cobre, DFT

Introdução. Em face da crescente necessidade do entendimento do mecanismo das reações químicas com o intuito de aumentar seu rendimento e eficiência em condições mais brandas, os catalisadores surgem como peças fundamentais na facilitação deste mecanismo.

Ante o exposto, a relevância deste estudo dá-se por se saber que muitas biomoléculas apresentam potencial atividade catalítica com aplicabilidade industrial, de modo que neste projeto sejam estudadas as propriedades de diversas sequências de aminoácidos e pequenos peptídeos, utilizando-se de simulações computacionais. A teoria empregada foi a teoria do funcional de densidade (DFT), a fim de se compreender a relação existente entre as propriedades exibidas pelas moléculas e seu potencial para atuar como catalisadores.

Neste projeto foram realizados estudos acerca da geração de estruturas, das propriedades termodinâmicas, geometrias e sítios de ligação presentes em pequenas sequências de aminoácidos e peptídeos quando complexados com íons de cobre, de forma a propor possíveis estruturas com atividade catalítica para reações REDOX. Mais especificamente, investigamos os complexos de Cobre(I) e Cobre(II) com a glicina, e com o peptídeo com sequência GHK (glicil-l-histidil-l-lisina).

Dentre as propriedades estudadas, estão ainda o potencial redox, a energia de reorganização e hidratação de diferentes configurações de alguns aminoácidos e pequenos peptídeos complexantes de cobre no vácuo e em solução aquosa.

Metodologia. A metodologia para geração de estruturas neste projeto é feita através de um protocolo sequencial que emprega o uso de *strings SMILES* (Simplified Molecular Input Line-Entry System), geração de estruturas 3D, cálculos semi-empíricos e da Teoria do Funcional da Densidade de maneira sequencial.

Estruturas iniciais são geradas usando o SMILES e o algoritmo gen3D, como implementado no código *openBabel*. Espera-se estender o protocolo utilizado aqui para cálculos *high throughput*, onde se consegue uma geração de milhares de estruturas a partir de um curto intervalo de tempo e baseando-se

em um *scaffold* previamente definido por uma string SMILES.

Estruturas iniciais foram primeiramente otimizadas com o método semi-empírico GFN2-xTB e posteriormente com o método DFT. Empregamos os funcionais PBE (Perdew-Burke-Ernzerhof), pertencente a classe GGA (aproximação de gradiente generalizado) e WB97x-D3, desenvolvido por Head-Gordon et al, pertencente a uma classe de funcionais denominada de *range-separated*.

Quanto às bases utilizadas, as escolhidas foram bases 6-31G(d,p) e tzvp (triple zeta valence potential) por apresentarem boa concordância com resultados experimentais para este tipo de sistema que estamos estudando.

Resultados. Dentre os resultados obtidos até o momento, os cálculos foram todos realizados tanto utilizando o funcional PBE como o WB97x-D3 nas bases 6-31G(d,p) e tzvp. Foi possível concluir que, para o caso do bisglicinato de cobre, sua geometria preferencial é quadrado planar, seguindo a configuração trans. Além disso, verificamos a região onde há maior tendência de permanência preferencial do próton, o que se deu no grupo amino bilateral em relação ao centro de cobre.

No caso do peptídeo GHK (glicil-l-histidil-l-lisina), obtivemos como geometria preferencial, uma geometria tetraédrica distorcida, onde o centro de cobre encontra-se envolto por dois nitrogênios advindos do grupamento imidazol da histidina e pelo oxigênio oriundo do backbone da lisina. Encontramos também um outro conformero de geometria tetraédrica onde, ao invés de encontrarmos como ligante o oxigênio do backbone, uma molécula de água da solução serve como ligante.

Os resultados obtidos revelam que o método semi-empírico GFN2-xTB produz geometrias próximas a dos funcionais DFT, sendo a diferença entre os resultados PBE e WB97x-D3 pequena. Adicionalmente, verificamos que o protocolo utilizado para produzir geometrias dos complexos de cobre com aminoácidos e peptídeos é eficiente e passível de automatização. Resultados para energias de reorganização e potenciais redox serão apresentados e comparados com os da literatura.



Comparing Transition Potential and Linear Response TD-DFT Methods to Simulate X-ray Absorption Spectra for CO Desorbing from Ru(0001)

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Keywords: XFEL, XAS, TD-DFT

Introduction

A fundamental problem in surface science is the exact nature of the bond between a given adsorbate and the surface. This problem has been extensively investigated by means of core-level spectroscopies due to its site-specific excitation mechanism and sensitivity to the local valence electronic structure at the core-excited atom¹. Specifically, X-ray absorption spectroscopy (XAS) is able not only to identify specific adsorbates on a surface but to differentiate the same species in different sites². Complementary, the combination of modern intense femtosecond optical lasers, with free-electron X-ray lasers (XFEL) has made it possible to follow the progress of chemical reactions in real time, allowing experimental probing of short-lived processes, such as desorption, c. As example, Figure 1 shows experimental⁴ XAS from a CO molecule desorbing from a Ru(0001) surface from a pump and probe experiment where we can see the evolution of the C1s $\rightarrow\pi^*$ peak while CO goes from a chemisorbed (unpumped) to a close-to-gas-phase state (8 to 10ps), with proper diminishing of π^* energy.

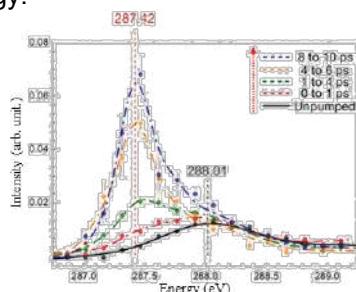


Figure 1: Carbon K-edge XAS from CO desorbing from a Ru(0001) surface. Figure adapted from reference⁴.

Despite all the progress, often the experimental results can be hard to interpret, e.g., if there are numerous species at the surface or if transient states are probed for which no steady-state reference is available. Thus, theory and accurate computational methods are needed to fill the gaps and give necessary information for an extensive description^{5,6}.

Objectives and Results

In the present work, we apply linear-response TD-DFT, using different functionals, to investigate the use of metal clusters of different sizes to simulate XFEL experiments monitoring CO vertical desorption from a Ru(0001) surface through XAS^{3,4}. Comparison is made with a more traditional transition potential

method within the Kohn—Sham orbital formalism (DFT-TP)⁵.

From Figure 2 we find that all calculated peak shifts of chemisorbed CO compared to gas phase are in the correct direction, albeit deviated from experimental value of +0.59⁴. As the Ru-CO distance is increased, we find the expected decrease in π^* energy, but with an overshoot from the gas phase value in both DFT-TP approaches, being attenuated in the periodic calculation. We ascribe this to charge-transfer from the metal to screen the charge on the molecule due to the removal of a half electron from the C 1s. In contrast, TD-DFT calculations do not suffer from this problem whilst showing satisfactory description of intermediate states as well of the two endpoints.

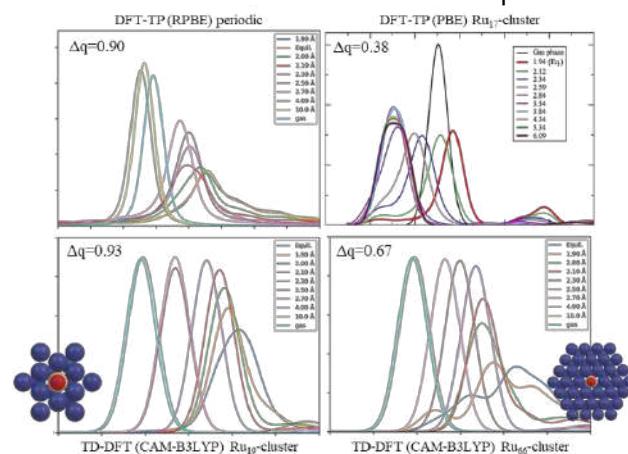


Figure 2: Calculated carbon K-edge XAS and chemisorbed to gas-phase chemical shifts (Δq). Clusters from bottom spectra are illustrated besides their respective spectra set.

Conclusions

In this work we showed that a linear-response approach, with TD-DFT and extended-clusters is as a viable option to simulate XAS evolution of a species desorbing from a metallic surface. It can be an alternative to DFT-TP, in systems where artificial charge transfers are a problem or transient species are poorly described. As next steps, we aim to apply more accurate wavefunction-based methods to this cluster approach.

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Difference of Kaolinite's facets behavior towards ions studied by Molecular Dynamics

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Palavras-Chave: Kaolinite, Electrolytes, Molecular Dynamics Simulation

INTRODUCTION

Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is the main gangue mineral present in iron ore processing slimes. It is a very important clay mineral in environmental and industrial fields. This phyllosilicate presents a hydrogen-bonded layered structure, as well as two facet parting terminations: a gibbsite-like hydrophilic facet (fG), full of hydroxyl groups; and a siloxane hydrophobic facet (fS). Not only these facets behave differently towards water, they also behave differently towards ions, even though the ideal theoretical structure and composition of these mineral surfaces are charge-neutral. In this work we assess such behavior by means of classical molecular dynamics simulations.

METHODS

Equilibrium molecular dynamics (EMD) simulations were run for each facet in contact with NaCl solution (1000 waters and 10 Na^+ and 10 Cl^-). Steered Molecular dynamics (SMD) simulations were performed for Na^+ and Cl^- ions with each facet in vacuum in order to obtain energy-distance profiles. All simulations were performed with LAMMPS software and CLAYFF forcefield [1].

RESULTS AND DISCUSSION

Table 1 shows the ion-surface interaction energies from EMD. We can note that the sign changes according to ion and surface pairs. The absolute values for fS are larger and very close to one another, while the values for fG are not as large and differ by ~ 12 kcal/mol \cdot nm 2 . Similar trends were observed for SMD simulations when the ion is far from the surface. These results demonstrate the difference in the mid-to-long range charge interaction of kaolinite's facets.

Table 1. EMD interaction energies (kcal/mol \cdot nm 2).

Ion\Surface	fS	fG
Cl^-	129.044	-95.215
Na^+	-130.569	83.109

SMD results showed the interaction profiles in Figure 1. At fS surface, Na^+ adsorbs preferentially between two oxygen sites, while Cl^- adsorbs atop Si sites. By forcing them closer to the surface, both adsorb at the

central region of the hexagonal ring-like structures. At fG surface, ion adsorption is led by the adjustment of hydroxyls' relative position and hydrogen bonding pattern. Cl^- preferentially adsorbs atop a hydrogen triangle, while Na^+ adsorbs at the center of a hydroxyl triangle where the hydrogens are pointing outward. The size of the ions also plays a major role. Na^+ is small enough so it can penetrate into the surface sites, this can be seen by the smaller value of z in the minimum of energy. Cl^- is large, and cannot benefit from the same effect. The difference in behavior seems to come from the position of the partial charges on the z axis. In fS, the oxygen atoms dominate the outer region of the surface, while in fG, hydrogen contribute more.

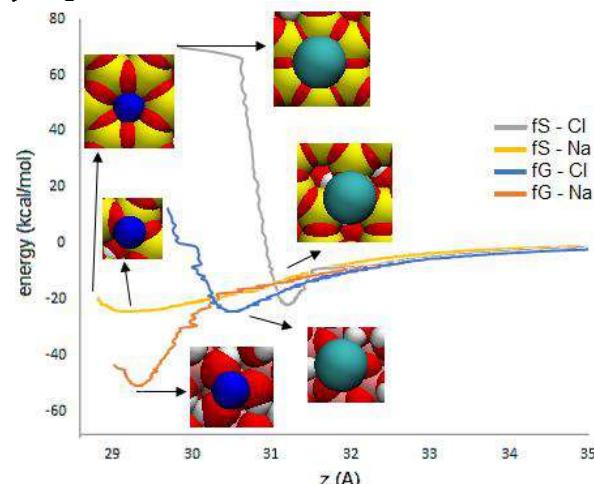


Figure 1. Potential energy curves and adsorption sites.

CONCLUSIONS

The siloxane facet has a dominant mid-to-long range negative character, while the gibbsite-like facet has a positive one. At close range, the partial charges and the arrangement of the surface sites as well as the ions' sizes modulate the adsorption energy and location of the ions.

ACKNOWLEDGMENTS

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Elucidação computacional do mecanismo molecular da abstração de hidrogênio do H₂S por radicais metilhalogenados.

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Palavras-Chave: Química atmosférica, Sulfeto de Hidrogênio, Teoria do Funcional de Densidade.

INTRODUÇÃO

O sulfeto de hidrogênio (H₂S) é um dos principais compostos contendo enxofre encontrados na atmosfera a partir de fontes antropogênicas e naturais¹, sendo um gás fundamental para o clima e flora do planeta². Pal e Subramanian³ demonstrou que radicais metilhalogenados podem ser importantes removedores de H₂S na atmosfera, levando a formação do radical mercapto (SH)². Os radicais metilhalogenados podem ser formados a partir da fotólise e das reações com os radicais OH[·], Cl[·] e NO₃[·]^{3,4}. Estes radicais metilhalogenados quando oxidados são extremamente reativos. Assim, no presente estudo foi caracterizado, via cálculos de estrutura eletrônica, o mecanismo molecular da abstração de hidrogênio do H₂S através de radicais metilhalogenados CH_{3-n}Cl_n[·] e CH_{3-n}Br_n[·] avaliando a influência da halogenação.

METODOLOGIA

Os mecanismos reacionais foram investigados com o método wB97xD/aug-cc-pVTZ. O caminho da reação foi confirmado por cálculos IRC (*intrinsic reaction coordinate*). No refinamento das energias eletrônicas, utilizou-se o método CCSD(T)/CBS a partir das bases aug-cc-pVQZ e aug-cc-pVTZ. Todos os cálculos foram realizados no programa Gaussian09.

RESULTADOS

Nas figuras 1 e 2, estão presentes os mecanismos das reações CH_{3-n}Cl_n[·]+H₂S e CH_{3-n}Br_n[·]+H₂S (n=1-3) descrevendo os processos de abstração de hidrogênio. Examinando os complexos de entrada formados entre as moléculas dos reagentes, a maior estabilidade foi observada nas estruturas que possuem dois (-2.1 kcal/mol) e três bromos (-2.7 kcal/mol). Entre os estados de transição (TS), as maiores barreiras de energia em relação aos reagentes são apontadas pelas reações que envolvem três cloros e três bromos com alturas de 6.5 e 4.7 kcal/mol, respectivamente. Entre os complexos de saída, os que apresentaram maiores energias de dissociação são as reações envolvendo CH₃Cl, CH₂Br₂ e CHBr₃. Além disso, os valores de variação de entalpia das reações variaram de -8.7 a -14.5 kcal/mol, indicando que todas as reações são exotérmicas. Já analisando a variação da energia

livre de Gibbs, todos os valores foram negativos, o que evidencia a espontaneidade da reação.

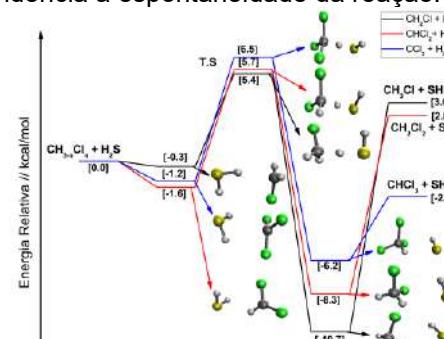


Figura 1 – As reações de abstração de hidrogênio CH_{3-n}Cl_n[·]+H₂S.

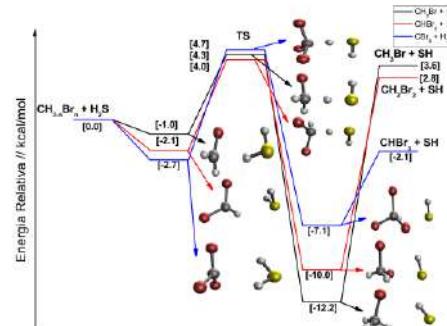


Figura 2 – As reações de abstração de hidrogênio CH_{3-n}Br_n[·]+ H₂S.

CONCLUSÕES

Considerando as pequenas barreiras, o caráter exotérmico e espontâneo das reações, os resultados indicam a possibilidade destas reações ocorrerem na troposfera.

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Properties of Laurixamine and Lauramidopropyl Dimethylamine surfactants in aqueous medium studied by Molecular Dynamics and DFT

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Palavras-Chave: Solvation, Amine Surfactants, Molecular Modeling

INTRODUCTION

Etheramines are the main type of collectors in iron ore flotation, but they need to be used alongside polysaccharide depressant agents, to guarantee the selectivity in separation of the iron minerals from silicates. The separation efficiency decreases when the silicate minerals contain Fe or Mg because their surface properties are similar to iron oxides'. The amidoamine Lauramidopropyl Dimethylamine has shown promising results in iron ore fines reverse flotation without the use of depressants [1]. In this work we compared solvation properties of this surfactant to a classical etheramine (laurixamine) used in industry, in neutral and protonated forms. The following convention applies: A – amidoamine, E – etheramine, (0) – neutral, (+) – protonated.

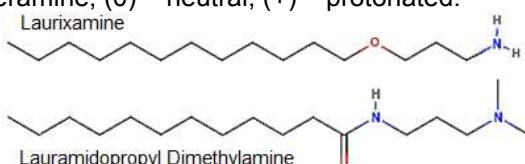


Figure 1. 2D structures of the studied amines.

METHODS

B3LYP/6-311++G(2d,p) with SMD solvation DFT calculations were performed using GAMESS software to obtain dipole moment (μ), HOMO-LUMO gap (H-L gap) and solvation free energy (ΔG_{solv}). All-atom equilibrium classical molecular dynamics simulations were performed using LAMMPS with SPC and CVFF forcefields to obtain properties such as radius of gyration (R_g), Solvent Accessible Surface Area (SASA), water-surfactant interaction energy (Esw), as well as studying solvation structure.

RESULTS AND DISCUSSION

An order of $E(+)<A(+)<A(0)<E(0)$ was observed for ΔG_{solv} and Esw, and of $E(+)>A(+)>A(0)>E(0)$ for μ and R_g . Although SASA is strongly related to solvation, the order of overall size was observed, $A(+)>A(0)>E(+)>E(0)$, contrasting to the other results. That indicates that, in this case, this property is more affected by the molecular size than the polarity. For the H-L gap, the values for both protonated species are quite similar, but the difference of the neutral

forms is more pronounced, especially for A, for which the value of this property increases in 1.08 eV while for E it only increases 0.21 eV on protonation.

Table 1. Summary of properties studied in this work.

		Etheramine		Amidoamine		units
	Charge	0	+1	0	+1	e
MD	Esw	-37.76	-115.71	-53.61	-108.49	Kcal/mol
	SASA	539.05	552.50	599.75	621.39	\AA^2
	R_g	4.28	5.95	4.69	5.15	\AA
DFT	μ	3.03	45.09	4.24	36.80	Debye
	H-L gap	6.54	6.75	5.75	6.83	eV
	ΔG_{solv}	-3.37	-63.28	-6.85	-52.03	Kcal/mol

Although the ether group is well solvated, the amide group is even more. In neutral form, both head and middle chain groups contribute in a similar manner to the overall solvation, but protonation makes the headgroups much more relevant.

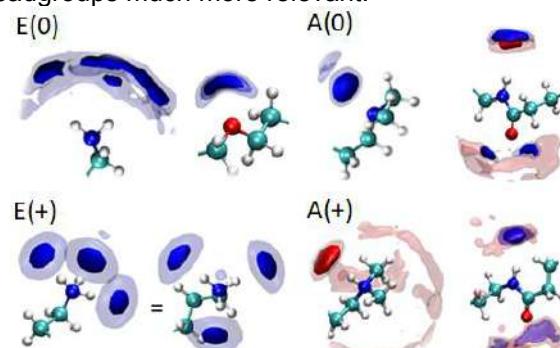


Figure 2. Spatial Distribution Functions of water.

CONCLUSIONS

The protonated amines interact more strongly with water, as expected. Comparing the neutral species, the amidoamine interacts better with water than etheramine, but the order is reversed on protonation, probably because it occurs at a primary amine site for E and at a tertiary amine site for A.

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Species Favorability and Methodology Approximations for the Zn:D2EHPA System

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Palavras-Chave: Solvent Extraction, Organometallics, Molecular Modeling.

INTRODUCTION

Extractive metallurgy is constantly seeking to achieve purer species and recover them from secondary sources. Organophosphorus compounds are applied for this objective. Years ago, the European Federation of Chemical Engineering (EFCE) proposed the extraction of zinc by the cation exchanger di-(2-ethylhexyl) phosphoric acid (D2EHPA) as a standard test system for equipment design. However, the chemical nature of the complex formed in high loading conditions is still obscure. In this work, we investigate the relative favorability of the complexes ZnL_2 and Zn_2L_4 using DFT. L stands for the cation exchanged D2EHPA.

METHODS

The two studied complexes were modeled with the original organic radical (2-Ethylhexyl: D2EHPA) and with a reduced one (propyl: DPHPA). DFT B3LYP/6-31G** calculations were performed using ORCA software [1]. Grimme's corrections (gCP-D3) were applied in thermochemical results [2]. We calculated the RMSD between the D2EHPA and the DPHPA complex based systems (Root-mean-square deviation of atomic positions) regarding only the central structure (atoms Zn, O, P). The Gibb's free energies for the theoretical isodesmic complex growth reaction: $2 ZnL_2 \rightarrow Zn_2L_4$ were compared.

RESULTS AND DISCUSSION

We obtained the RMSD values of 1.32 \AA between the two ZnL_2 complexes and 0.23 \AA for the Zn_2L_4 ones, comparing each D2EHPA based complex (Figure 1) with their reduced forms (DPHPA-based).

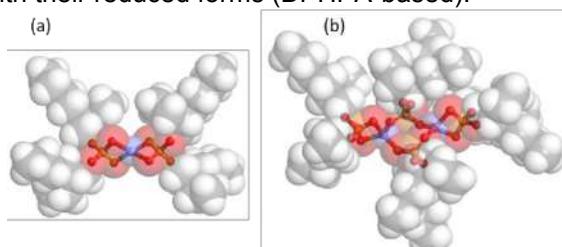


Figure 1. Complexes' structures. (a) ZnL_2 (b) Zn_2L_4 .

In structural biochemistry, a value of 3 \AA is a good similarity threshold for RMSD in proteins [3], so we adopted a value of 1.5 \AA for our complexes, since they are much smaller. Therefore, both complexes have adequate geometry, however the bigger complex shows a better similarity, which is related to the more relaxed and stable 8-member ring structure. Table 1 shows Gibb's free energy, the mean absolute error (MAE), and the relative error (% Error). The D2EHPA based corrected value is considered the standard, and it indicates that the Zn_2L_4 complex is more favorable by $\sim 42 \text{ Kcal}\cdot\text{mol}^{-1}$. The corrected DPHPA model shows minor errors indicating that if the gCP-D3 correction is applied, the reduced system becomes a valid approximation.

Table 1. Gibb's Energies in $\text{Kcal}\cdot\text{mol}^{-1}$ values and respective errors.

L in the complex	ΔG	MAE	% Error
D2EHPA Corrected	-42.05	0	0.00
D2EHPA	-30.75	-11.30	26.86
Non-Corrected			
DPHPA Corrected	-39.72	-2.33	5.54
DPHPA	-33.48	-8.57	20.39
Non- Corrected			

CONCLUSIONS

DFT B3LYP/6-31G** results showed that the Zn_2L_4 complex is more favorable than ZnL_2 . The DPHPA based complex could acceptably reproduce both thermochemistry and structure of the D2EHPA based complex. However, Grimme's corrections should be used to achieve more accurate results.

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Método de Runge-Kutta de 4^a ordem para a equação de Schrödinger estacionária com energia zero

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Palavras-Chave: Runge-Kutta, confinamento, energia zero.

INTRODUÇÃO

A equação de Schrödinger estacionária pode ser estudada em seu modo zero de energia, o que permite o estudo do estado limite de ligação de uma partícula¹. Em uma abordagem extrínseca do confinamento de uma partícula em uma região unidimensional² (curva), o Hamiltoniano possui, além do termo de energia cinética, um termo de energia potencial, dependente da curvatura da curva. O método Runge-Kutta de quarta ordem pode ser aplicado para a solução numérica do modo zero da equação Schrödinger estacionária aplicada ao confinamento unidimensional.

METODOLOGIA

No tratamento extrínseco a equação de Schrödinger para o modo zero de energia de uma partícula confinada é dada pela expressão:

$$\frac{\partial^2 \Psi(s)}{\partial s^2} = -\frac{k(s)^2}{4} \Psi(s) \quad (1)$$

Onde s é a variável de comprimento de arco, $\Psi(s)$ a função de onda e $k(s)$ é a curvatura da curva.

Dada uma EDO de segunda ordem, o respectivo sistema de EDOs de primeira ordem, nas variáveis x, y e z com suas condições iniciais pode ser obtido³:

$$\begin{cases} y' = z \\ z' = g(x, y, z) \\ y(x_0) = y_0 \\ z(x_0) = z_0 \end{cases}$$

O método de Runge-Kutta de 4^a ordem pode então ser aplicado da seguinte maneira:

$$y_{i+1} = y_i + \frac{h}{6}(l_{1y} + 2l_{2y} + 2l_{3y} + l_{4y}) \quad (2)$$

$$z_{i+1} = z_i + \frac{h}{6}(l_{1z} + 2l_{2z} + 2l_{3z} + l_{4z}) \quad (3)$$

Onde, l_{1y} e l_{1z} são inclinações no início do intervalo estudado, l_{2y}, l_{3y}, l_{2z} e l_{3z} são inclinações na metade do intervalo, l_{4y} e l_{4z} são inclinações no fim do intervalo e h é o passo escolhido para o método.

RESULTADOS

Além dos casos canônicos de uma partícula confinada num intervalo de reta e em um círculo, foram obtidas as soluções numéricas de $\Psi(s)$ para as curvas espiral de Arquimedes e espiral Logarítmica, respectivamente $k(s) = \frac{2}{\sqrt{s}}$ e $k(s) = \frac{4}{s}$. As funções

de onda tiveram um comportamento senoidal, porém apresentaram um aumento da amplitude e do comprimento de onda.

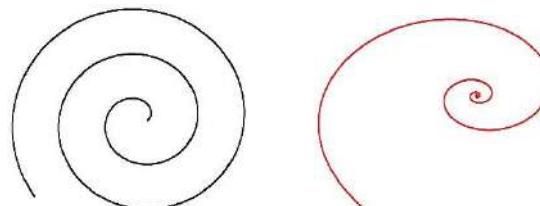


Figura 1. Esboço das curvas espiral de Arquimedes (—) e espiral Logarítmica (—).

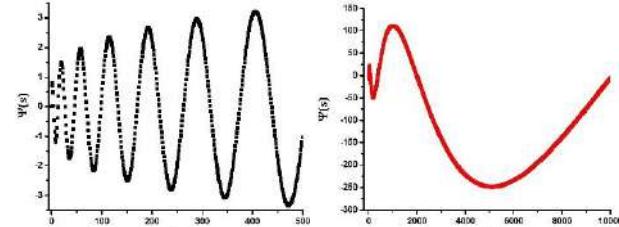


Figura 2. $\Psi(s)$ nas espirais de Arquimedes (—) e Logarítmica (—).

A densidade eletrônica é maior na região de menor curvatura, localizando nesta os estados mais fracamente ligados. Este resultado está de acordo com a previsão de Da Costa na sua formulação extrínseca de confinamento. As funções de onda tendem a 0 com $s \rightarrow L$ (comprimento final da região de confinamento). Este resultado indica que os elétrons mais ionizáveis em uma molécula ou nanoestrutura devem se encontrar nas regiões de menor curvatura.

CONCLUSÕES

Resolvemos numericamente a equação de Schrödinger estacionária para o problema do modo zero no confinamento extrínseco de uma partícula nas espirais de Arquimedes e Logarítmica. Os resultados demonstram que moléculas ou nanoestruturas com essas geometrias tendem a ter seus elétrons ionizáveis em suas regiões com menores curvaturas.

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Estudo sobre indicadores espectroscópicos das substâncias tóxicas do Hg(II) na natureza.

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Palavras-Chave: Mercúrio, Espectroscopia, Cinética.

INTRODUÇÃO

O mercúrio é um metal que possui um histórico de uso desenfreado pela sociedade. Cotidianamente a população humana utilizava este metal em diversos produtos necessários para a vida moderna, tais quais: lâmpadas fluorescentes, termômetros, medicamentos, pilhas e baterias. Em 2017, o Brasil assinou a Convenção de Minamata sobre o mercúrio, ocasionando no Projeto de Lei 8911/17 – atualmente arquivada – que estipulava a eliminação do estoque do mercúrio metálico e seus compostos, com medidas ecológicas até o ano de 2020¹. O motivo da existência das leis e convenções ocorre pelo fato de existir compostos com alta toxicidade à vida animal no ciclo global biogeoquímico do mercúrio. Ao decorrer do ciclo podemos notar que a emissão de $Hg(0)_{(g)}$ na atmosfera será oxidado, produzindo $Hg(II)_{(g)}$ e acarretando na produção de halatos de mercúrio $HgBr_2$, $HgCl_2$, entre outros. Ao serem precipitados junto a chuva e depositados no oceano, uma das principais reações que ocorre: a metilação do mercúrio, gera um dos compostos mais tóxicos aos humanos, o mono metilmercúrio H_3C-Hg^+ .² Este trabalho então possui o objetivo de gerar dados espectroscópicos teóricos das substâncias consideradas mais importantes. As moléculas escolhidas para a criação desse banco de dados espectroscópicos teórico foi baseado nas principais possibilidades de formação e de bioacumulação, tanto na atmosfera quanto no oceano. Sendo assim, estudou-se o $XHgY$ ($X, Y = CH_3, OH, Br, Cl, I, O_2H$) na possibilidade de formação dos mesmos na atmosfera, criando assim uma base de dados para possíveis mapeamentos ecológicos do mercúrio. O espectro de absorção também auxilia no entendimento da conversão fotoquímica $Hg(II) \rightarrow Hg(0)$.

METODOLOGIA

Os cálculos de otimização de geometria, hessianas e frequências das moléculas escolhidas foram feitas em RASSCF/ANO-RCC-VTZP usando o hamiltoniano relativístico Douglas-Kroll-Hess de 3^a ordem no programa OpenMolcas³. O espaço ativo é composto por 12 elétrons e 12 orbitais. O espectro de absorção foi obtido de forma semiclássica, com uma amostragem baseada na distribuição de Wigner, usando o programa SHARC2.1⁴. Nesta etapa os cálculos de estrutura eletrônica foram feitos em MS-CASPT2.

RESULTADOS

O espectro de absorção para uma das moléculas calculadas, na faixa de energia entre 0 – 40 eV, é mostrado na figura 1. Nesta faixa a absorção ocorre majoritariamente entre 5,5 – 6,1 eV. Nota-se que as contribuições para o espectro são apenas para os três primeiros estados excitados singletes.

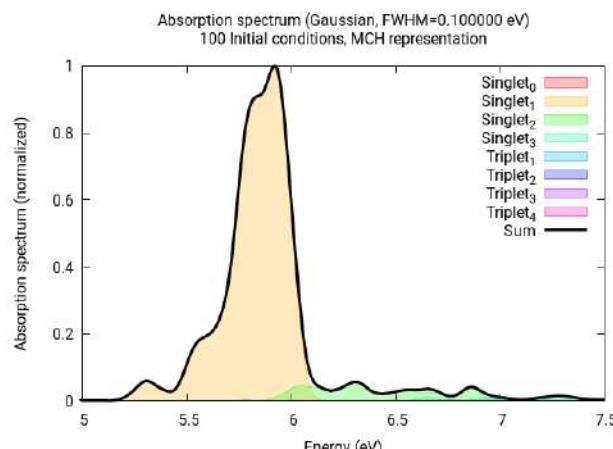


Figura 1: Espectro de absorção do Dimetilmercúrio.

CONCLUSÕES

O método de pesquisa se mostrou altamente eficaz para os objetivos deste trabalho, tendo sido possível calcular os espectros de absorção das espécies de interesse. Foi possível avaliar a influência dos ligantes X e Y no espectro de absorção das espécies do $XHgY$.

AGRADECIMENTOS

Agradeço a UFF e a CAPES pelo suporte à pesquisa.

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pyPolyBuilder: An automated software to create molecular topologies and initial configurations of arbitrary supramolecules for molecular dynamics simulations.

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Keywords: Molecular Dynamics, Molecule Building, Topology Building

Introduction

Several areas of nanotechnology require specific development of molecular engineering in order to fulfill the technological demand. An usual technique of choice for studying large systems are the molecular dynamics (MD) simulations.¹

However, in order to carry a MD simulation out, some initial information are required. For instance, the initial coordinates and the molecular topology file (MTF) of the system. Those files tend to be cumbersome to build by hand. For larger systems, it become unpractical. There are some topology builders² available in the literature, but as far as we know, the options are focused on building smaller molecules or a specific structure (e.g., proteins and high-branched polymers).

Methods

To avoid human errors and to make the process of preparing initial configurations and initial topology easier and faster, we developed the pyPolyBuilder: An general automated software for building topologies of large molecules.

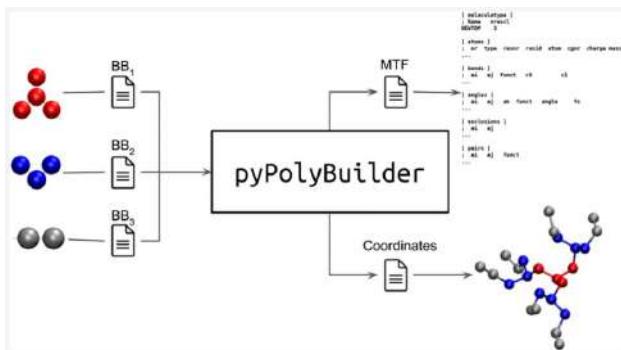


Figure 1: Schematic workflow for pyPolyBuilder³

PyPolyBuilder³ algorithm is based on smaller pieces of MTFs named as building-blocks (BB) (See Figure 1). To make the software as general as possible, those BBs are connected in accordance to a connectivity file defined by the user. For the purpose of BBs linkage, we developed an object-oriented framework using the python language in which each atom, bond, angle and dihedral angle is modeled as

a distinct object. Hence, it supported us to handle the complexity of managing several building blocks.

Results

Figure 2 shows some selected complexes molecules built using pyPolyBuilder. Both systems were then solvated and simulated for a few nanoseconds (data not shown). Those and several other examples are available in pyPolyBuilder repository.

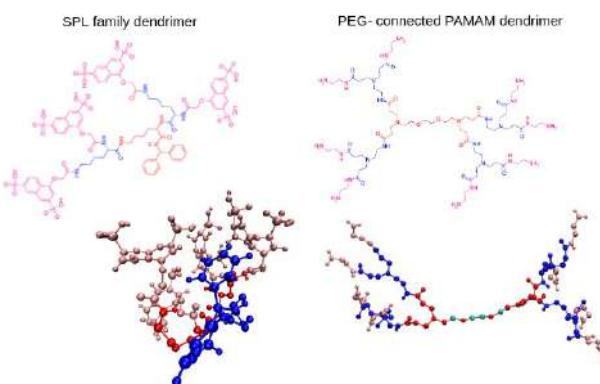


Figure 2: Illustrative examples of complexes molecules built using pyPolyBuilder. Left panel: a smaller version of the SPL7013 dendrimer of generation 1. Right panel: a modified PAMAM dendrimer in which the core BB was allongated using a PEG polymer.

Conclusions

PyPolyBuilder is a flexible, versatile, easy to use and computer efficient software developed to build arbitrary supramolecular structures. Its standalone approach makes it easy to be used in any workstation. Further improvements and extensions for different MD engines and force fields will make it even more powerful and useful.

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NACAD/COPPE/UFRJ, CAPES, CNPq, FAPERJ and the European Union's Horizon 2020 research and innovation program (no. 764958)



Estudo teórico do efeito solvente em sondas fluorescentes

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Palavras-Chave: Modelagem molecular, Efeito Solvente, QM/MM, Espectroscopia

INTRODUÇÃO:

O Laurdan (6-dodecanoil-2-dimetilaminonaftaleno) é uma sonda fluorescente amplamente usada no estudo de sistemas biológicos como bicamadas lipídicas e membranas celulares. Neste trabalho, estudamos essa molécula e os efeitos de solventes de diferentes polaridades com um enfoque físico e computacional. A comparação com os resultados experimentais [1] e teóricos [2] foi realizada para validar nossos modelos.

METODOLOGIA:

Utilizamos cálculos de mecânica quântica (QM) e simulações atomísticas com mecânica molecular (MM) com campo de força clássico para descrever, no primeiro momento, as interações intramoleculares do Laurdan e, no segundo momento, as interações intermoleculares da sonda com os solventes. Usamos métodos de DTF para os cálculos quânticos de carga e dos espectros de absorção do Laurdan e, para as simulações do Laurdan solvatado, usamos modelos de solventes orgânicos discretos.

RESULTADOS:

Primeiramente, usamos simulações de dinâmica molecular (MD) do Laurdan no ensamble NVT em vácuo para analisar as propriedades estruturais da sonda e validar o campo de força (GAFF) usado nas simulações subsequentes.

Após essa etapa de validação, realizamos uma análise de *benchmarking* de seis funcionais e duas bases de funções com cálculos QM do tipo TD-DFT das três primeiras excitações eletrônicas do Laurdan. Constatamos que B3LYP/6-31G(d) e M062x/6-311G(d) se mostraram as melhores combinações de funcional e base para reproduzir os resultados experimentais.

Em seguida, fizemos simulações MD do Laurdan solvatado em ciclohexano (CHX, baixa polaridade) e em metanol (MOH, alta polaridade) no ensamble NPT. Nelas, usamos dois conjuntos de cargas atômicas do Laurdan: do campo de força GAFF e de cálculos com o método CHelpG no modelo contínuo (PCM) dos solventes.

Com 100 configurações extraídas das trajetórias, calculamos as excitações eletrônicas do Laurdan tratando os solventes como um campo eletrostático gerado pelas cargas pontuais dos átomos nos cálculos TD-DFT. A partir da convolução lorentziana dos resultados, construímos os

espectros teóricos, cujos picos se encontram na Tabela 1 junto com os resultados experimentais.

Tabela 1: Valores calculados do número de onda (10^3 cm^{-1}) do pico da 1a banda do espectro de absorção do Laurdan e o deslocamento solvatocrômico (Shift) correspondente. Resultados experimentais são mostrados para comparação.

Método	Cargas	CHX	MOH	Shift
B3LYP/ 6-31G(d)	GAFF	26.7	26.1	-0.6
	CHelpG	26.9	24.9	-2.0
M062x/ 6-311G(d)	GAFF	30.2	29.8	-0.4
	CHelpG	30.4	28.7	-1.7
Exp. [1]	-	29.1	27.3	-1.8

CONCLUSÕES:

Concluímos que as cargas atômicas do campo de força GAFF (não polarizadas devido a presença do solvente) não são capazes de reproduzir o solvatocromismo experimental de CHX → MOH no valor de $-1.8 \times 10^3 \text{ cm}^{-1}$. Por outro lado, o modelo teórico com as cargas atômicas CHelpG (implicitamente polarizadas pelo solvente) mostra claramente que o solvatocromismo no espectro do Laurdan depende diretamente da polarização do solvente. Além disso, o método M062x/6-311G(d) se mostrou mais adequado para descrever esses efeitos.

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Fragmentation Route of doubly ionized benzene, aniline and nitroanilines monomers using a novel protocol from density functional theory

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Palavras-Chave: *doubly charged, Theory of Bader, Fragmentation Route.*

INTRODUCTION

The studies of mass spectrometry (EM) are focused on the analysis of the fragmentation of species present in the ionosphere of extraterrestrial planets that, in their states of charge 2+ (doubly charged), which suggests a possible way of molecular fragmentation.^[1] To connect the theory to the experiment, we calculated the electronic structure of the molecules, using a new working protocol applied to the amino acid cysteine in a recent publication^[21], benzene (BZ), aniline (ANI), and the nitroanilines (NA) in conformations *ortho*-, *meta*- and *para*- (named oNA, mNA, and pNA, respectively) for the neutral species, and doubly ionized to infer the dynamics of fragmentation of these molecules.

METHODOLOGY

All our calculations of first principles of quantum mechanics were performed using the Gaussian software (release 09)^[2] applied to the molecular structure of the benzene, aniline, o-, m-, and p-nitroaniline, at different levels (neutral, and ions), the existing basic formalism of B3LYP method with a basis set of Dunning type aug-cc-pVDZ. Also, we determined the topological properties by applying QTAIM^[3] for the electronic structure.

RESULT

The theoretical calculations of the electronic structure of the BZ, ANI, and NA molecules show the effect of double ionization on the chemical bonds of -CC- and the groups -NH₂ and -NO₂; when we remove two electrons from the neutral molecules.

These different isomeric conformations lead to the stabilization of the system in the molecular ion (BZ²⁺, ANI²⁺, oNA²⁺, mNA²⁺, and pNA²⁺) doubly ionized. The BZ molecule is in the plane and symmetrical, unlike of BZ²⁺, which has two carbon atoms outside the plane. The effect of double ionization in molecules that have the -NH₂ amine group causes the hydrogen atoms to be in a single molecular plane and have different angles between carbon-nitrogen and bisect the H-N-H angle, as in the case of the aniline molecule. From the Wiberg's binding order and Bader's theory were defined the connections between lower charge concentrations and breaking chemical bonds.

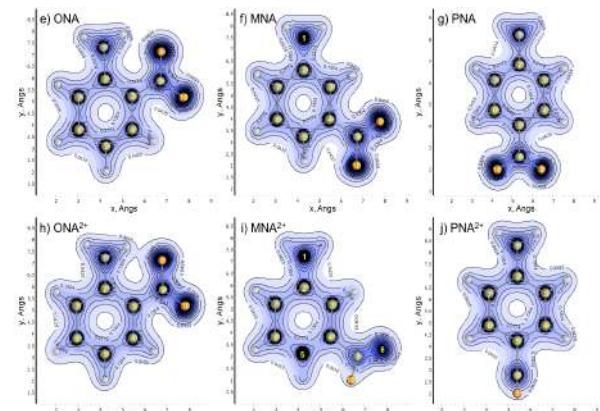


Figure 1. Electronic density maps in the plane of the atoms N-C, -C-C- and O=N=O for nitroanilines in e) ONA, h) ONA²⁺, f) MNA, i) MNA²⁺, and g) PNA, j) PNA²⁺.

Therefore, with the relaxation of the system, the charge distribution is altered (figure 1), thus leaving some pairs of atoms weaker than the others and this can be seen in the electronic density maps, represented graphically for neutral and doubly ionized species.

CONCLUSION

The investigation of a theoretical molecular fragmentation route may be possible through the application of two methods: Wiberg's bond indexes and Bader's topological analysis (QTAIM). The fragmentation route lead to the indication of weakened bonds due to the removal of two electrons from the system.

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The JOYSpectra web platform for luminescence of lanthanides

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Keywords: Lanthanide spectroscopy; web platform; intramolecular energy transfer.

Introduction

Lanthanide-based materials are applied as luminescent markers, dosimeters and nanothermometers, for instance, due to the unique photophysical and optical properties of the trivalent lanthanide ions (Ln^{3+})¹. Several works have been developed to rationalize and predict such properties, especially, 4f-4f transition intensities, radiative and non-radiative intramolecular energy transfer (IET) (ligand-Ln) and Ln-Ln energy transfer processes². In this sense, we have developed a web platform for calculating the luminescent properties of Ln-based compounds, named JOYSpectra (JS).

About the JS web platform

The JS is a free-of-charge website hosted in CCA/UFPB (<http://slater.cca.ufpb.br/joysspectra/>) were theoreticians and experimentalist can obtain information on the intensity parameters (Ω_λ) and IET rates. The Ω_λ calculation include covalency effects and the IET rates are calculated from excited donor states for several Ln^{3+} transitions.

The JS front-end was developed in PHP and HTML and takes as input the geometry of the Ln-based material in cartesian coordinates or from Gaussian, Orca or MOPAC output files. The user geometry can be observed on the website due to the JSmol API. Then additional information is requested to the user dependent of the calculation type, such as experimental Ω_λ , charge factors, ligand effective polarizabilities, temperature, donor energy, for instance. After build the online input, the calculation is performed on dedicated computers and the results are sent by email.

The JS also provided an online output viewer where the user may observe the main results of its calculation and, if the IET rates were requested, a Jablonski-type diagram of highest contributions.

Illustrative Example: $[\text{Ln}(\text{tta})_3(\text{H}_2\text{O})_2]$

In this example, Ln stands for Eu^{3+} and Tb^{3+} and tta for the thenoyltrifluoroacetone. Experimentally, this europium compound exhibits a reasonable emission³ while the terbium compound presents a strong luminescence quenching⁴. We considered that both complexes are isostructural and used the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ geometry available under the CCDC code: 758487a. The charge factors, ligand effective polarizabilities were provided for an Ω_λ fitting calculation and the spectroscopy data for S_1 and T_1

donor states were provided to perform the IET calculation. All data used in this example are available in reference 5 and in JS for the user perform the calculation by themselves.

The intensities parameters Ω_2 , Ω_4 and Ω_6 were calculated for the Eu complex, for instance, as 33.05, 8.17 and $1.45 \times 10^{-20} \text{ cm}^2$, respectively, and agree with the experimental values.

From the JS output viewer, the highest rates contributing for IET are present and may be downloaded as *png* or vectorial *pdf* (Figure 1). For this example, the JS calculation showed the $T_1 \rightarrow ^5D_1$ as the largest IET path for the Eu compound, and for Tb complex the $S_1 \rightarrow ^5G_6$. It is noticeable that the Tb complex the backward rates are larger than forward ones, indicating the quenching character of tta in this complex.

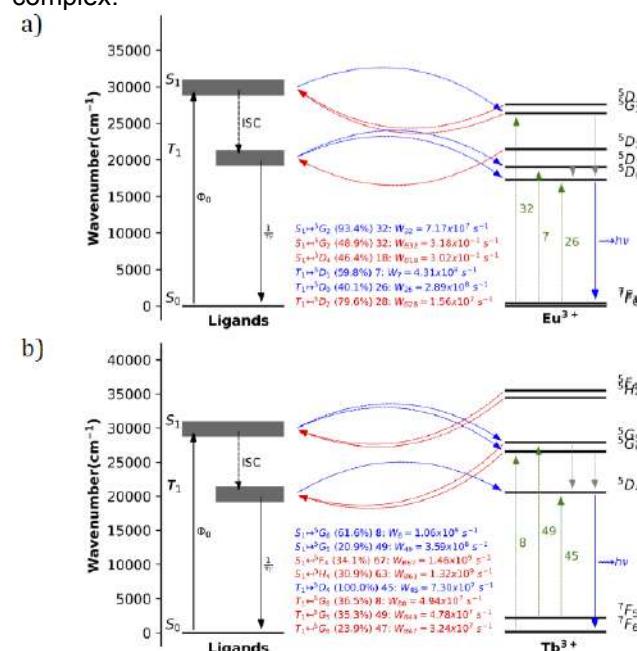


Figure 1. Jablonski-type diagrams for the studied coordination compounds.

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SiC monolayer as promising anode material for sodium-ion batteries

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Palavras-Chave: grafenileno, SiC, SIBs, anodo, DFT.

INTRODUCÃO

Derivado do grafeno, o grafenileno (GP) possui nanoestrutura com poros simetricamente distribuídos e com promissora aplicação em armazenamento de energia¹. À vista disso, análogos inorgânicos com estrutura do tipo GP têm sido empreendidos e suas propriedades avaliadas, o qual é o caso do grafenileno inorgânico do tipo SiC (IGP-SiC), estrutura semicondutora investigada neste estudo como possível anodo em baterias de íons-sódio (SIBs).

METODOLOGIA

As simulações foram conduzidas com a Teoria do Funcional da Densidade (DFT) aplicada a sistemas periódicos, e assim combinadas com o funcional híbrido B1WC e funções de base *all-electron*. Os cálculos computacionais dessas simulações foram executados com o auxílio do software CRYSTAL17.

RESULTADOS

A saturação de Na no IGP-SiC deu-se primeiramente nos anéis hexagonais, cujos sítios são mais estáveis energeticamente. A diferença de densidade de carga de um único átomo de Na no hexágono está registrada na Figura 1a, onde percebe-se um acúmulo de elétrons (cor amarela) nas ligações do hexágono adsorvido e altas regiões de depleção (cor azul) pela monocamada, indicando assim que o Na está atuando como doador de elétrons, o que é desejado para processos de carga e descarga em baterias.

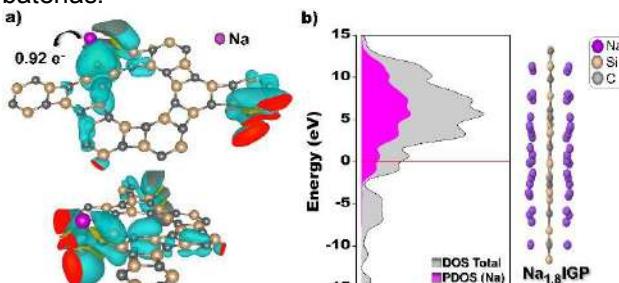


Figura 1: a) Diferença de densidade de carga para o átomo de Na adsorvido no anel hexagonal. b) Visualização lateral e densidade projetada (PDOS) para o sistema Na@IGP de maior capacidade de armazenamento.

Testou-se o armazenamento de Na no IGP-SiC a fim de aferir sua capacidade máxima, com os átomos de sódio sendo inseridos sobre e sob a monocamada para aproveitar a simetria do sistema. Chegou-se a adsorção máxima de 44 átomos de sódio, o que representa a proporção Na_{1,8}IGP (Figura 1b). Nota-se pelas Figura 2A e 2B que com o aumento da saturação de Na, a energia de adsorção torna-se

mais negativa e há maior transferência de carga, conforme visto pela PDOS da Figura 1b, evidenciando o processo de fisissão nos sistemas Na@IGP. Além disso, avaliou-se que a proporção máxima de Na (Na_{1,8}IGP) indica uma capacidade específica de 597,52 mAh.g⁻¹ (Figura 2C), valor superior aos encontrados para outros materiais 2D, tais como grafeno (308 mAh.g⁻¹)² e fosforeno (324 mAh.g⁻¹)³.

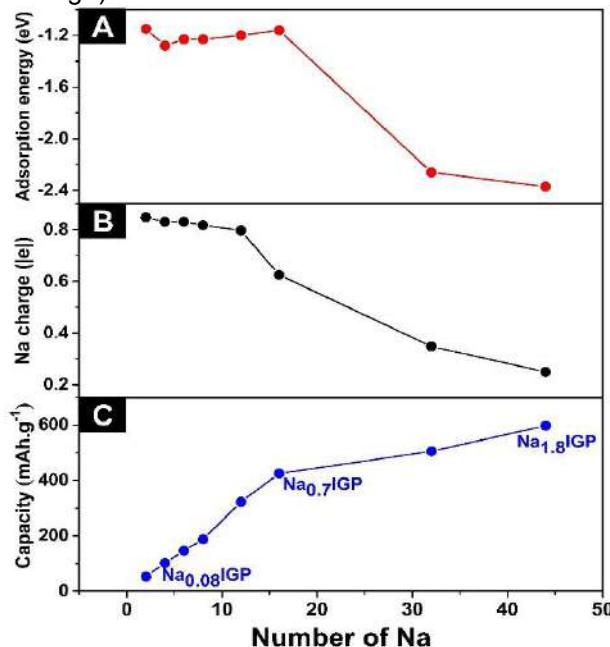


Figura 2: (A) Energia de adsorção (eV), (B) Carga do Na (|e|) e (C) Capacidade (mAh.g⁻¹) dos sistemas Na@IGP.

CONCLUSÕES

O IGP-SiC apresenta-se como um promissor anodo de SIBs, visto sua alta capacidade específica e mínima distorção estrutural após adsorção. Além disso, a monocamada assume caráter condutor com a presença dos átomos de sódio, indicando a doação de elétrons do Na para a estrutura porosa e assim facilitando o processo de carga e descarga em baterias da próxima geração.

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Estudo Computacional de Complexos Octocoordenados e Nonocoordenados $[\text{Tb}(\text{RP})_2(\text{H}_2\text{O})_n(\text{Cl})_{x-n}]$.

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Palavras-Chave: Complexos de Térbio, Púrpura de Ruhemann.

INTRODUÇÃO

O Púrpura de Ruhemann (RP) é um produto da reação entre a ninidrina e aminoácidos utilizado na revelação de impressões digitais latentes¹. Estudos experimentais reportam que o RP age como sensibilizador da emissão de íons lantanídeos, no entanto, não são apresentados dados estruturais do complexo responsável por essa emissão². Recentemente, dados de intensidade experimentais foram utilizados para sugerir o complexo responsável pela emissão no sistema Eu-RP, através de estudos teóricos de suas propriedades luminescentes³.

Desta forma, aplicamos esta metodologia para propor a geometria do complexo mais provável pela emissão observada no sistema Tb-RP considerando as espécies presentes no sistema experimental: TbCl_3 , RP e H_2O .

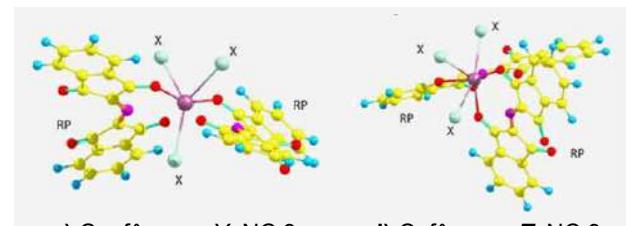
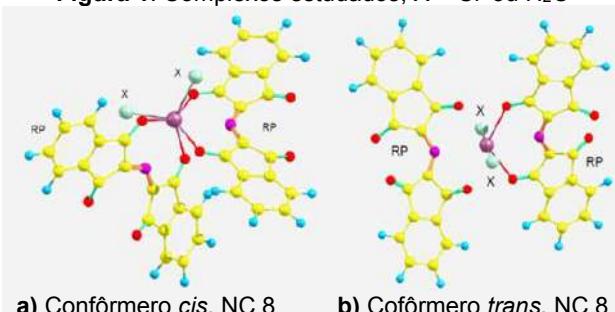
METODOLOGIA

Os complexos $[\text{Tb}(\text{RP})_2(\text{H}_2\text{O})_n(\text{Cl})_{x-n}]$ foram avaliados com $x = 2$ ou 3 e $n = 0, 1, 2$ e 3 para o número de coordenação (NC) 8 e 9. Ao todo, foram obtidas 18 estruturas possíveis. Todos os complexos e ligantes isolados foram totalmente otimizados com o funcional wB97X-D3 e conjunto de base def2-TZVP, o ECP MWB54 foi aplicado para descrever o $\text{Tb}(\text{III})$, e o CPCM para simular o solvente metanol (MeOH) de maneira implícita.

RESULTADOS

A forma geral dos complexos é apresentada na Figura 1. As denominações *cis* e *trans* referenciam as posições relativas dos ligantes X (Cl^- ou H_2O), bem como a designação *Y* e *T* nos complexos com NC 9 representam o posicionamento destes ligantes X.

Figura 1. Complexos estudados, X = Cl^- ou H_2O



c) Confôrmero *Y*, NC 9

d) Cofôrmero *T*, NC 9

Para complexos com NC 8 os confôrmeros *cis* se mostraram mais estáveis que seus isômeros *trans* devido a repulsões estéricas nos grupos carbonila. A estabilidade nesses complexos também aumenta com o número de ligantes *cloro*, tendência também observada em complexos Eu-RP³. Para os complexos com NC 9 não foi observada preferência entre confôrmeros *cis* ou *trans*, entretanto, complexos em *T* se mostraram ligeiramente mais estáveis que complexos em *Y*, com exceção ao $[\text{Tb}(\text{RP})_2\text{Cl}_3]$ onde o isômero *Y* é relativamente mais estável que o *T*. O complexo mais estável foi o *trans*- $[\text{Tb}(\text{RP})_2(\text{H}_2\text{O})\text{Cl}_2]-T$, que no conjunto estudado apresentou população Boltzmann relativa igual a 99,77%.

Moura Jr. e colaboradores⁴ mostraram que as taxas de transferência intramolecular de energia (IET) destes complexos são da mesma ordem de grandeza, 10^9 para S_1 e 10^7 para T_1 , e concordam com a observação experimental do singuleto atuar como canal principal, sendo o complexo *cis*- $[\text{Tb}(\text{RP})_2(\text{H}_2\text{O})\text{Cl}]$ aquele com maior IET.

CONCLUSÕES

Complexos com NC 8 se mostraram preferência pela conformação *cis*. Complexos com NC 9 mostraram preferência pela conformação em *T*. O complexo mais estável obtido foi o *trans*-912-T sendo este o mais abundante e provável responsável pela luminescência observada no sistema experimental.

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AGRADECIMENTOS

UFRPE.



CONFINAMENTO ELETRÔNICO EM HPAs

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Palavras-chave: equação de Schrödinger, partícula confinada, HPA.

INTRODUÇÃO

Os hidrocarbonetos policíclicos aromáticos (HPAs) são moléculas com dois ou mais anéis benzênicos geminados e possuem em sua estrutura elétrons π ressonantes. Estudando a equação de Schrödinger através de métodos teórico-analíticos e computacionais podem ser previstas várias de suas propriedades [1]. O modelo da partícula confinada também pode contribuir para o melhor entendimento do espectro UVV desses sistemas.

METODOLOGIA

Foram elaborados modelos moleculares para os seguintes HPAs: benzeno, naftaleno, antraceno, tetraceno, pentaceno, hexaceno, heptaceno, octaceno, nonaceno e decaceno. Considerando cada parte fechada da molécula como uma respectiva região de confinamento dos elétrons π , cada uma pode indicar respectivas transições eletrônicas. As moléculas foram otimizadas com o método AM1 e seu espectro UVV obtido pelo método ZINDO, ambos implementados no programa Gaussian 09.

Os resultados foram comparados com dados experimentais presentes na literatura. [2]

RESULTADOS

Foi possível encontrar diversas transições $\pi \rightarrow \pi^*$ dentre outras para os HPAs tanto com o método analítico quanto computacional. A quantidade de regiões de confinamento (R) conseguiu explicar parte do número de picos do espectro experimental (P). A massa efetiva (m^*) referente ao valor exato das transições eletrônicas foi encontrada e comparada com valores utilizados para nanoestruturas e sólidos [3].

Tabela 1: Comparação dos resultados

R	P	Sistema	λ_{Teo}	λ_{Com}	λ_{Exp}	m^*/m_e
1	6	Benzeno $6\pi^-$	192	199	179	1,03
3	10	Naftaleno $6\pi^-$	195	234	220	1,14
		Naftaleno $12\pi^-$	280	293	275	1,49
5	10	Antraceno $6\pi^-$	196	262	252	1,29
		Antraceno1 $0\pi^-$	394	367	375	1,33
7	*	Tetraceno $10\pi^-$	197	286	274	1,45
		Tetraceno $14\pi^-$	391	439	473	2,23

8	10	Pentaceno $14\pi^-$	455	507	580	2,10
9	*	Hexaceno $10\pi^-$	326	335	325	1,02
		Hexaceno $14\pi^-$	456	427	678	1,47
10	*	Heptaceno $10\pi^-$	397	387	380	0,97 2
		Heptaceno $14\pi^-$	600	625	657	1,12
11	*	Octaceno $10\pi^-$	327	370	*	1,13
		Octaceno $14\pi^-$	525	530	*	2,29
12	*	Nonaceno $10\pi^-$	327	390	*	1,19
		Nonaceno $14\pi^-$	526	570	*	2,45
13	*	Decaceno $10\pi^-$	330	423	*	1,23
		Decaceno $14\pi^-$	457	466	*	1,01

* Resultados não encontrados na literatura

A quantidade das regiões de confinamento dos elétrons π ajudou na previsão do número de picos do espectro UVV das moléculas de HPAs. Além disso, foi possível prever o comprimento de onda das principais transições tanto analiticamente quanto computacionalmente. O estudo da massa efetiva necessita de um maior aprofundamento incluindo sistemas bidimensionais de HPAs. Esse modelo pode ser testado para outros HPAs contendo heteroátomos e até mesmo ajudar na previsão do espectro de novas moléculas.

CONCLUSÕES

Os modelos moleculares e de confinamento eletrônico conseguiram prever algumas propriedades do espectro UVV de HPAs. Os resultados concordam com dados experimentais encontrados na literatura.

A previsão de espectros UVV destes sistemas pode ser uma perspectiva.

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AGRADECIMENTOS

UFRPE e LnP



Theoretical elucidation of the enantioselectivity of proline containing lipopeptides

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Keywords: Lipopeptides, Aldol reactions, Computational Chemistry

L-proline and their derivatives have been used as promising catalysts in aldol reactions for stereoselective carbon-carbon bond formation. Both computational and experimental results led to the accepted Houk-List mechanism, in which an intramolecular hydrogen transfer is a critical factor in promoting the reaction.

Recently, studies addressed new types of catalysts in which a carboxylic acid group is absent, such as L-prolinamides and proline-containing peptides and lipopeptides. The latter can self-assemble in solution generating new morphologies whose chemical environment ranges from hydrophilic, aqueous at their surface, to hydrophobic inside the complex moieties. Lipopeptides with sequences PRWG-C₁₈ and PRWG-(C₁₈H₃₇)₂ (where P stands for proline, R to arginine, W to tryptophan, G do glycine) have been shown experimentally to form aggregates with various topologies and exhibit catalytic properties towards a model aldol reaction between p-nitrobenzaldehyde (PHA) and cyclohexanone (CHN). In this work, we investigate using Molecular Dynamics (MD) and Density Functional Theory (DFT) fundamental aspects of these systems that can influence their catalytic activity, especially their efficacy in producing compounds with high enantiomeric excess.

Molecular dynamics using AMBER and the AMBER family of force fields (ff14SB and lipid14) revealed a layered structure for PRWG-C18 and PRWG-(C₁₈H₃₇)₂, where catalytic proline stays at the interface region with about half the water content when compared to the bulk. A critical step in defining stereochemistry is the enamine proline (ENP) and p-nitrobenzaldehyde (PHA) intermediate complex pair formation. We used MD to characterize their appearance and investigate if the aggregate environment favors complexes with different prochiral arrangements.

The classical MD simulations showed that reactants with (S,R) and (S,S) pro chirality arrangement are more abundant when compared to (R,R) and (R,S), suggesting that the micellar phase can promote specific prochirality when compared to simulations in pure cyclohexanone (in which a micellar phase is not formed).

Catalytic barriers for the stereoselective step were investigated using Density Functional Theory (DFT), the B3LYP-D3 functional, and the Nudged Elastic Band Climbing Image(NEB-Cl) methods on an N-methyl-L-prolinamide model compound. In addition, solvent effects were included using the SMD method employing a cyclohexanone medium to model the micellar environment. Moreover, we investigate whether trifluoroacetic acid (TFA), commonly used in aldol reactions and present in the environment as a counterion, can actively participate in the reaction. All DFT calculations were performed using the Orca code v 4.1.

Our results indicate that TFA can act as a proton donor in a proton relay mechanism, facilitating the reaction. In addition, the transition state approximation results (from NEB) exhibit different C-C bond lengths depending on the attack face, suggesting that TFA's role can influence the mechanism synchronicity. We also found that the reaction barriers can be affected by ring stacking at the transition state. Configurations with PHA stacked on top of five-membered rings had barriers for the *anti* (S,R) product at 1.77 kcal/mol and the *syn* (R,R) and (S,S) products at 3.07 and 2.51 kcal/mol, respectively. The barriers for configurations with PHA stacked on top of the six-member ring were 2.29 kcal/mol for the *syn* (S,S), 4.49 kcal/mol for the *anti* (S,R), 6.28 kcal/mol for the *syn* (R,R) and 8.52 kcal/mol for the *anti* (R,S) configurations. Our results agree with experiments that had the (S,R) and (S,S) stereoisomers as the most abundant species.

Taken together, results from our DFT and molecular dynamics simulations indicate that the high enantiomeric excess observed in experiments when using proline-containing lipopeptides are a result of intrinsic mechanistic features and properties from the microstructured environment provided by the micellar medium.



Estudo cinético da abstração de hidrogênio nas reações de inicialização de combustão

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Palavras-Chave:Modelo cinético, biodiesel, ésteres metílicos, combustão

Introdução

O biodiesel é um combustível de origem vegetal e que se apresenta como uma alternativa para a redução do uso de combustíveis de fontes não renováveis. Um grande problema da modelagem cinética do biodiesel é a quantidade de reações no modelo cinético de combustão [1]. Por este motivo é proposto o estudo da combustão de ésteres metílicos de cadeia curta para aprimorar modelos de combustão do biodiesel [3], e estudos teóricos das reações de abstração de hidrogênio ligadas a ignição do biodiesel. Dessa forma, o presente estudo visa estudar as reações de abstração de hidrogênio do etanoato de metila (EM) usando métodos *ab initio* e DFT associados à teoria do estado de transição.

Metodologia

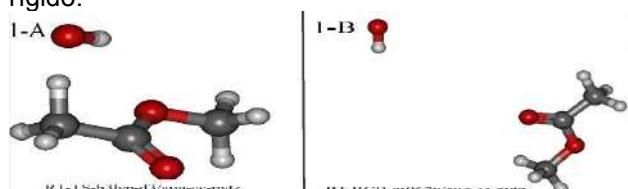
As reações estudadas foram a abstração de um hidrogênio do EM feita pelas seguintes espécies: OH (R1), O₂ (R2), OH₂ (R3), O (R4) e H (R5). Inicialmente, foram otimizadas as geometrias dos reagentes produtos e estados de transição usando a teoria do funcional da densidade. Foram utilizados os funcionais híbridos B3LYP-D3 e M062X, na base aug-cc-pVTZ.

Os cálculos de estrutura eletrônica e parâmetros termodinâmicos foram feitos usando o Gaussian 16 [2]. Os parâmetros cinéticos foram calculados a no intervalo de 298 K a 3000K e 1 atm via teoria do estado de transição convencional e variacional.

Resultados e Discussão:

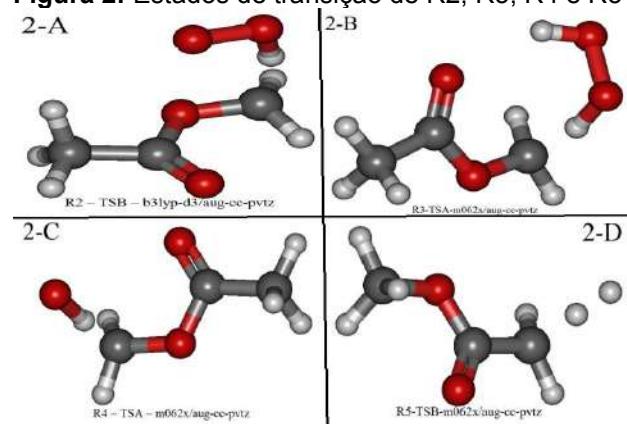
Após a otimização e o cálculo da barreira da reação, notou-se que a reação com o radical OH passa por um complexo pré-barreira Figura 1A). O caminho de reação para formação deste complexo foi construído através de um scan rígido para descrever o afastamento do radical OH do EM, com passo de 0,2 Å (Figura 1B representa os fragmentos separados).

Figura 1. Estruturas para R1 pré-barreira e scan rígido.



A Figura 2 ilustra alguns dos estados de transição otimizados para as outras reações.

Figura 2: Estados de transição de R2, R3, R4 e R5



A Tabela 1 apresenta as equações de Arrhenius obtidas para cada reação estudada em nível M06-2X/aug-cc-pVTZ.

Tabela 1. Coeficientes de velocidade obtidos

	m062x	
	In(a)	m
		Ea
R1A	-9,38	-2,77
R1B	-16,02	-2,45
R2	-53,08	4,55
R3	-57,09	4,62
R4	-42,39	3,36
R5	-41,62	3,24

Posteriormente, os resultados obtidos serão comparados com dados na literatura.

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Exploring H₂ adsorption over Cu-SSZ-13 through finite cluster models

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Keywords: zeolites, hydrogen storage, DFT.

In this work, we have explored the adsorption of H₂ over Cu-containing SSZ-13 zeolite using as a model a hydrogen-capped finite cluster and atom-centered basis sets. Our approach contrasts with the most commonly reported treatment of solids such as zeolites, which employ plane-wave basis sets and periodic boundary conditions in order to account for long-range interactions originated from the extended zeolite structure.

The behavior of our 78-atoms, 16 T-sites model (figure 1) was first explored through a benchmark of DFT methodologies (B3LYP, B3LYP-D3(BJ), M06L, PBE, PBE-D3(BJ) and ωB97XD) and the use of the def2-SVP basis set.

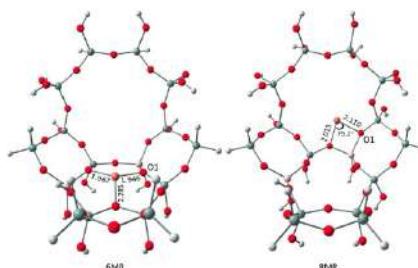


Figure 1: Cluster for Cu(I)-SSZ-13 with Cu loaded at the 6MR (left) and 8MR (right) with 78 atoms. Geometries obtained with the B97X-D/def2-SVP method. Color code: O in red, Si in grey, Al in light pink, Cu in orange and H in white.

In every case, two different locations for the Cu(I) cations and the H₂ adsorption were studied: the 8-membered ring and the 6-membered ring.

Geometries resulting from optimizations were compared with experimental neutron diffraction data for D₂ adsorption over Cu-SSZ-13 and calculated enthalpies, using thermal corrections obtained after frequency calculations at structural local minima, were compared to those obtained experimentally.

The wave function provided by the methodology that better reproduced experimental results in terms of both geometry and adsorption enthalpy – ωB97XD, table 1 – was later used for a wide-ranging study of

and Quantum Theory of Atoms in Molecules (QTAIM) analyses. Furthermore, the resulting geometry was studied with the gold-standard DLPNO-CCSD(T)/def2-TZVP methodology (table 2), which also made possible a Local Energy Decomposition study.

Our study has demonstrated the viability of the use of a relatively small cluster model of only 78 atoms and 16 T-sites, which is able to capture adsorption enthalpies, and in turn allow the use of highly-accurate methodologies for the description of the electronic density which would be unpractical for more computationally-expensive systems, such as full-periodic calculations. Such a wide-ranging analysis was able to point out the localized nature of the H₂-zeolite and Cu-zeolite interactions, which are dominated by the local geometry of zeolite rings, as previously inferred by experimentalists, without however reaching a settlement.

Fundamentally, the hindered location of the Cu(I) cation at the 6-membered ring makes it unavailable to interact with H₂, resulting in the lower 3.8 kcal/mol adsorption energy. In contrast, the Cu(I) cation located at the 8-membered ring has lower-lying available orbitals, raising the stabilization of the adsorbed H₂ molecule, which is further stabilized by non-covalent interactions with the zeolite ring. The overall result is a tripling of the adsorption energy to 11.5 kcal/mol. As demonstrated by the LED analysis, in both cases interactions are dominated by non-dispersive terms, pointing, once again, to the decisive role of the zeolite as a ligand to the Cu(I) cation, and the reduced role of long-range interactions.

Table 2: H₂ adsorption at 6MR and 8MR. Experimental enthalpy values(ΔH_{exp}), calculated with ωB97XD functional values ($\Delta H_{\omega\text{B97XD}}$), electronic energies calculated at the DLPNO-CCSD(T)/def2-TZVP level of theory($\Delta E_{\text{DLPNO-CCSD(T)}}$) and calculated enthalpy energies corrected with CCSD(T) energies ($\Delta H_{\text{corr}}^{\text{DLPNO-CCSD(T)}}$). All values are given in kcal/mol.

Cluster	ΔH_{exp}	$\Delta H_{\omega\text{B97XD}}$	$\Delta E_{\text{DLPNO-CCSD(T)}}$	$\Delta H_{\text{corr}}^{\text{DLPNO-CCSD(T)}}$ ^a
6MR/H ₂	-3.8	-4.9	-4.2	-2.3
8MR/H ₂	-11.5	-14.9	-14.4	-11.3

^a $\Delta H_{\text{corr}}^{\text{DLPNO-CCSD(T)}} = \Delta E_{\text{DLPNO-CCSD(T)}} + H_{\text{corr}(\omega\text{B97XD})}$.

Reference

Phys. Chem. Chem. Phys., 2021, **23**, 9980

Table 1: H₂ adsorption enthalpies at 6MR and 8MR with different functionals. The experimental value for H₂ adsorption at the 6r is -3.8 kcal/mol and at the 8r is -11.5 kcal/mol

Cluster	B3LYP	B3LYP-D3 ^a	PBE	PBE-D3 ^a	M06L	ωB97XD
6MR	-2.4	-5.0	-5.4	-7.4	-6.5	-4.8
8MR	-6.4	-15.0	-21.5	-23.7	-24.1	-14.9

^a D3 is D3(BJ).



Improving selectivity in (electro)oxidation of polyols with Bi adatoms on Pt(111) surface

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Keywords: DFT, electrooxidation, electrocatalysis

Since the mid-1990s, biomass-derived energy sources have been explored as the world is looking for fossil-based fuels alternatives. This important renewable energy source is composed of C1 to C6 oxygenated species, from formic acid to sorbitol; some of them, such as glycerol, can be reactants to platform chemicals of industrial interest.

The employment of these species in (electro)oxidation reaction has been explored for several catalysts, including multimetallic alloys, metal oxides, nanoparticles and others. Among all, we highlight the extensive use of noble metals. Thus, Au, Pd and Pt can oxidize with efficiency. One particular interest is the modification of platinum surfaces with bismuth adatoms. Kimura et al.¹ reported the results of glycerol oxidation with bismuth incorporation to platinum supported on charcoal. They observed glyceraldehyde (GLD) and glyceric acid as the main oxidation products, both derived from the oxidation of the primary hydroxyl group. With bismuth addition, dihydroxyacetone (DHA) became the main oxidation product, generated from the oxidation of the secondary hydroxyl

group. The study proposed that Bi atoms work as site blockers on Pt surface and control the orientation of glycerol, resulting in the oxidation of the secondary hydroxyl group.

In this context, we performed DFT calculations, using the Vienna Ab initio Simulation Package (VASP). PBE and RPBE functionals were employed with and without dispersion corrections (D3). The double-dehydrogenated intermediates of glycerol and erythritol (Figure 1) were modeled to investigate the selectivity change of the polyol electrooxidation reaction with bismuth addition on Pt(111) surface. Our results demonstrate a significant reaction selectivity change in presence of Bi adatoms, favouring the oxidation of the secondary hydroxyl group in agreement with the experimental evidences.

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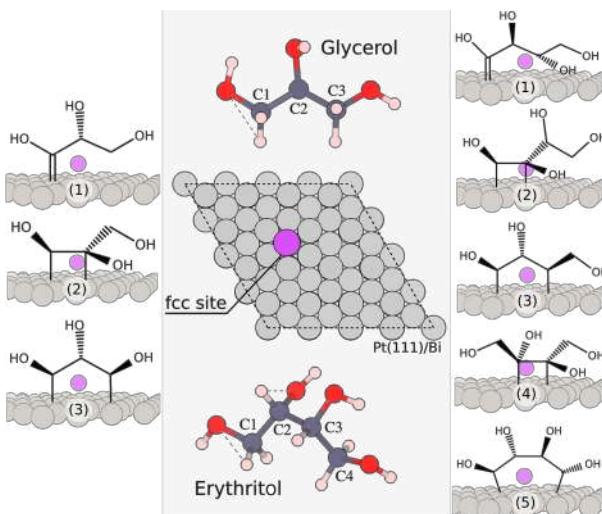


Figure 1: Scheme representation of the proposed glycerol and erythritol intermediates.



Calculation of Second Virial Coefficient using Ab Initio Intermolecular Potential Energy Surface for Dimer F₂···F₂

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Palavras-Chave: second virial coefficient, F₂···F₂, analytical potential energy surface.

INTRODUCTION

In the past few years we have been working in developing potential energy surface (PES) using the spherical harmonic expansion. To this end, we freeze the interatomic distance of each monomer at the equilibrium distance optimized for each basis set as a rigid rotor. This approach allows us to perform all necessary calculations with lower computational cost. In principal, the rigid rotor generates relatively good values for the second virial gaseous property in the interval of temperatures of interest. As a prototypical function for the analytical intermolecular potential we use the Pirani *et al.* potential function[1]:

$$V(R, \gamma) = \varepsilon \left[\frac{m}{n(R, \gamma) - m} \left(\frac{R}{R_m} \right)^{n(R, \gamma)} - \frac{n(R, \gamma)}{n(R, \gamma) - m} \left(\frac{R}{R_m} \right)^m \right]$$

where R is the distance between the centers of the monomers and $\gamma \equiv (\theta_1, \theta_2, \phi)$, according to the well known Jacobi coordinates. m, R_m, ε are a free parameter, minimum position of the well, and the depth of the well respectively. n(R, γ) is given by

$$n(R, \gamma) = \beta + \alpha \left(\frac{R}{R_m} \right)^2$$

where β e α are free parameters here. It has been proved that this prototypical function captures correctly the R⁻⁶ behavior of the potential. The anisotropy of the analytical PES is obtained through the spherical harmonics expansion using six Leading Configurations (LC) with the three fixed angles (θ_1, θ_2, ϕ): H($\pi/2, \pi/2, 0$), L(0,0,0), T($\pi/2, 0, 0$), S($\pi/3, \pi/3, \pi/2$), Z($\pi/4, \pi/4, 0$), and X($\pi/2, \pi/2, \pi/2$).

The spherical harmonics expansion includes the v⁴⁰⁴ moment, the is repulsive like the v²²⁰ moment. v⁰⁰⁰ is the isotropic term and can be measured experimentally. To our knowledge, there is no data for the second virial coefficient for F₂···F₂ system.

METHODOLOGY

In previous works, we studied the importance of molecular anisotropy in systems such as A₂···A₂[2] and A₂···X₂[3]. We use Molpro to calculate a set of 100 *ab initio* points at varying intermolecular distances 2.5 $\leq R \leq 12.5$ Å, for each LC, at the CCSD(T)/aug-cc-pVXZ level, with X = D and T, and

use the CBS extrapolation for the energies: $E_k = E_\infty - a/k^3$, with k = 2, 3 for DZ and TZ respectively. As a good test we perform calculations to obtain the second virial coefficient for such a system. The classical and the respective quantum corrections are given in the expansion

$$B_2(T) = [B_{cl}(T) + B_r^r(T) + B_I^{a,l}(T) + B_I^{a,\mu}(T) + \dots]$$

B_{cl} is the classical second virial coefficient. The other coefficients of the expansion are the radial and angular quantum corrections whose expressions can be found in our previous work [3].

RESULT

The most stable LC is the X, with energy of 17.4 meV and distance of 3.0 Å while the less stable is the L one with energy of 6.1 meV and distance of 4.3 Å. The equilibrium distance of the F₂ molecule was obtained at the same basis set level getting 1.418 Å. This result is in good agreement with the experimental data, i.e., 1.412 Å.

Van and Deiters construct two 5-site potential functions and were fitted with standard thermodynamic relations to obtain the second virial coefficients. In general, we can say these values are in satisfactory agreement with the Van and Deiters work [4] for this range of temperatures.

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XXI SBQT

DFT study of clofazimine and its interactions with the *p*-aminobenzoic acid coformer in the formation of an amorphous material

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Key-words: Density Functional Theory, Leprosy, Solid Dispersions.

INTRODUCTION

Clofazimine, a lipophilic rimonophenazine antibiotic, is a useful drug to treat leprosy and other disorders¹. This drug has low solubility in aqueous media, which can be adjusted using coformers to prepare solid dispersions, promoting a significant increase in the dissolution rate and bioavailability of the drug². The improvement of these properties contributes to the reduction of side effects in the oral use of the drug. Several theoretical methods are available in computational chemistry software and allow the obtention of several parameters that enable a better understanding of the properties and behavior of these chemical systems. We used Density Functional Theory (DFT)³, which has been widely used in studies of chemical systems, to the study electronic and structural properties of the drug clofazimine and the *p*-aminobenzoic acid coformer, as well as the its interactions between their ionic forms.

METODOLOGY

The theoretical study was carried out using the DFT functional ω B97x-D and the basis set 6-311++G(d,p), in the study of each compound and their ions, as well as for the drug-coformer interactions study. In addition, the solvation effect in each of the systems was studied using the IEFPCM solvation method. The representations of the chemical structure of the compounds were built using the *Chemcraft* software, and then the geometry optimization and vibrational frequency calculations were performed using the *Gaussian* software 16.

RESULTS

Structural, electronic, and thermodynamical properties of the compounds were determined firstly. From the next step, we designed the starting geometries for the study of the drug-coformer interactions, considering the most negative site of one of the ions next to the most positive site of the other, considering the basis set superposition error.

The results are presented in the Table 1 and Figure 1, shown below.

Table 1. Thermodynamic parameters calculated for CFZH⁺, PABA⁻ e CFZH⁺-PABA⁻ interaction

Calculation de ΔG ($\Delta G = G_{AB} - (G_A + G_B)$)	
Systems	G (kcal/mol)
CFZH ⁺	-1368905,1870
PABA ⁻	-298449,1209
CFZH ⁺ -PABA ⁻	-1667362,0790
ΔG	= -7,7715 kcal/mol
BSSE	= 0,0026 kcal/mol

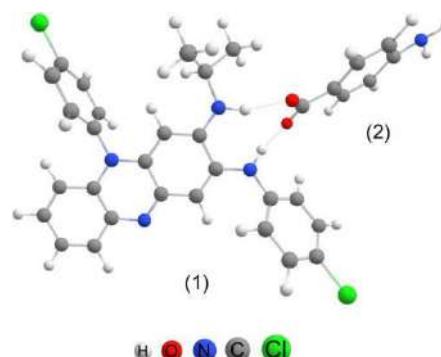


Figure 1. CFZH⁺-PABA⁻ interaction

CONCLUSIONS

This study is useful, contributing for the characterization of the materials studied and also to confirm the stabilization of the material formed by means of intermolecular forces between the ions.

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Study of the interactions between Trypsin with BTCl derived molecules

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Palavras-Chave: Docking, BTCl, Trypsin.

Introduction

Trypsin is an enterokinase that belongs to the S1 family of serine proteases, catalyzing the hydrolysis of specific peptide bonds after positively charged residues (Arg and Lys). The first reactive site of most dicot inhibitors inhibits trypsin, while the second inhibits trypsin, chymotrypsin and elastase [1].

BTCl is a globular protein of a polypeptide chain with 83 residues isolated from a BBI, the seeds of *Vigna unguiculata* (cv *Seridó*). [2] The interaction between BTCl and trypsin is mediated by many polar contacts and hydrogen bonds, Ser190, Gly193, Ser195 and Ser210 and a salt bridge between the Lys26, Asp189. [3]

Through the reactive structure of BTCl, a peptide formed by a chain of 9 amino acids, called ptry9, from Cys24 to Cys32 in the BTCl sequence, was selected. Their conformations are named as ptry9-D, for the D-amino acid conformation, and ptry9-L, for the L-amino acid conformation for the cysteine residues. Another related molecule was ptry6, which consists of a peptide reduced from the C-terminus of ptry-9, but the Ptry 6 peptide has this cyclicity broken. [4]

Methodology

The 3D structure of ptry9 was taken from 6E5M and 6EAT protein crystals, while PTRY6 was brought from 6EAX protein crystal using Discovery Studio Visualizer [5]. Hydrogen saturation was carried out using GaussView 4.1 software [6].

The structures of ptry6, ptry9-D, ptry9-L were optimized in vacuum and implicit (PCM) solvent using Density functional theory (DFT) with B3LYP functional using 6-31G and def2svp basis set were used. The calculations were performed using Gaussian09 package [7].

The docking was done using the 6E5M PDB structure, and all simulations were performed using the AutoDock 4 automating suite [8] and (VMD) software [9]. For visualization the results and interactions was used the Discovery Studio Visualizer [5].

Results

The simulation of catalytic hydrophobic process was realized with a docking without water, Table 1.

Table 1. Results of Molecular Docking of Trypsin with peptides.

No.	Proteína	Composto	Energia de Ligação (Kcal/mol)	Constante de Inibição (Ki)	No. de ligações de hidrogênio (ligante-enzima)
1.	6E5M	Ptry9-L sol	-16.05	0.17 nM	13
2.		Ptry9-L vac	-15.74	0.28 nM	12
3.		Ptry9-D sol	-15.27	0.64 nM	12
4.		Ptry9-L PDB	-15.18	0.74 nM	11
5.		Ptry9-D vac	-15.03	0.95 nM	9
6.		Ptry9-D PDB	-14.68	1.73 nM	9
7.		Ptry6 sol	-12.87	36.7 nM	2
8.		Ptry6 vac	-11.19	626 nM	2
9.		Ptry6 PDB	7.63		

Our results express same experimental inhibition sequence, where ptry9-L is the better inhibitors than ptry9-D and ptry-6. Figure 1, shown 2D and 3D interactions between Trypsin and ptry9-L inhibitor.

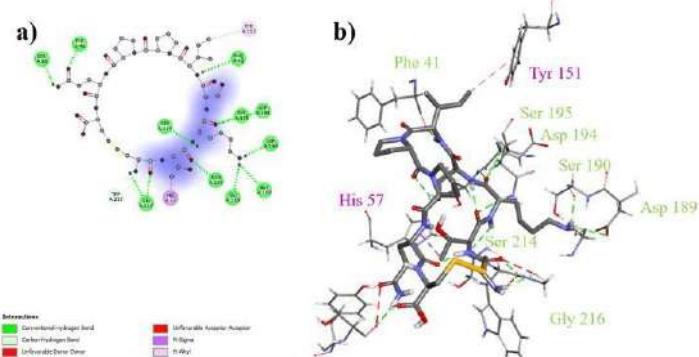


Figure 1. Ptry9-L docking with Trypsin. a) 2D interaction with residues b) 3D interaction with residues.

Conclusions

Through our experiments it was understood that ptry9-L interact with important residues of trypsin similarly to BTCl. The nature of those interactions has a higher energy than ptry9-D and ptry-6 complex with trypsin, those results are in head with in-vitro experiments.

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XXI SBQT

Estudo computacional de uma nanofolha porosa de grafeno como filtro para o gás SO₂.

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INTRODUÇÃO

Apesar da evolução da tecnologia, a utilização de motores a combustão interna ainda é amplamente utilizada globalmente e, devido ao seu uso crescente e contínuo, há a preocupação com a emissão de gases que geram poluição do ar e causam problemas de saúde na população (Reitz et al., 2020). Uma forma de minimizar esta poluição atmosférica é o constante desenvolvimento de materiais para atuação como filtros de gases poluentes. Há estudos sobre o uso de membranas de grafeno (e derivadas do grafeno) para a filtragem de gases, devido à sua resistência mecânica e estabilidade química (Jiao; Xu, 2015).

OBJETIVO

Nossa proposta para esse trabalho foi estudar a passagem de moléculas do gás poluente dióxido de enxofre (SO₂) através de uma nanofolha porosa de grafeno. Foram analisados mecanismos de filtragem, avaliando a adsorção de moléculas à superfície da nanofolha, considerando interações de van der Waals e de Coulomb, observando também a influência do tamanho do poro na nanofolha e da temperatura do sistema.

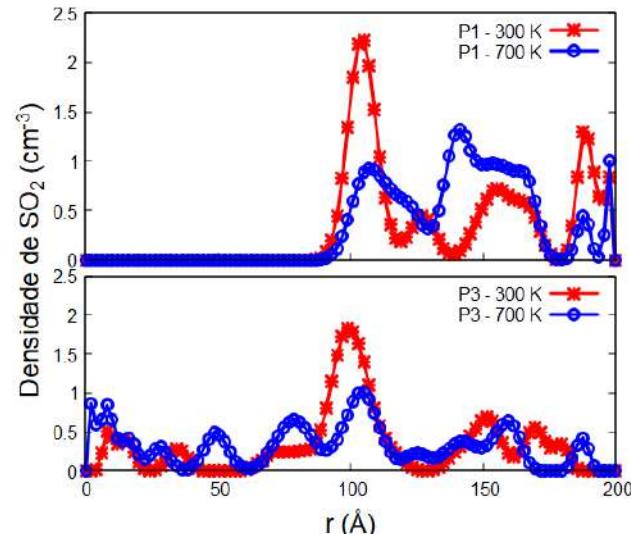
METODOLOGIA

Foram estudados três sistemas, todos contendo 24 moléculas de SO₂, e cada um com um tamanho diferente do poro na nanofolha de grafeno (15 Å², 40 Å² e 100 Å²). Para as simulações, consideramos uma caixa de simulação de dimensões X = 33 Å, Y = 34 Å e Z = 200 Å, com a nanofolha fixada em z = 100 Å, com seu plano paralelo ao plano xy, e as todas as moléculas de SO₂ inicialmente em somente um dos lados da caixa. A passagem das moléculas desse gás pelo poro presente na nanofolha foi avaliada para as temperaturas de 300 K, 500 K e 700 K, através da análise da densidade de partículas e da densidade radial de pares. O pacote LAMMPS foi usado para integrar as equações de movimento do sistema, considerando um timestep de 1,0 fs, em NVT, com a temperatura controlada pelo termostato de Nose-Hoover (Hoover, 1985). O tempo total de cada simulação foi de 5 ns, e as propriedades foram calculadas durante o último 0,5 ns. Para realização das simulações foi utilizado um campo de força classico do tipo CHARMM.

RESULTADO E DISCUSSÃO

A Figura 1 mostra os resultados para a densidade de partículas de SO₂, para as temperaturas de 300 K e 700 K, e para dois tamanhos de poro (P1 = 15 Å² e P3 = 100 Å²). Decorre dessa Figura que o tamanho do poro, assim como a temperatura, influencia diretamente a filtragem das moléculas, conforme esperado, e que há uma considerável concentração de moléculas de SO₂ próximas ao grafeno. Uma análise adicional da energia potencial do sistema como função distância entre SO₂ e grafeno, mostra a presença de um mínimo local de energia, sugerindo uma possível adsorção.

Figura 1. Densidade Gráfico de densidade da nanofolha de grafeno (A) 15 Å² (B) 100 Å².



CONCLUSÃO

De acordo com os resultados obtidos até o presente momento, pode-se afirmar que a efetividade no bloqueio da passagem de SO₂ aumenta para poros de tamanho não muito grandes e para temperaturas próximas à temperatura.

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Molecular dynamics investigation of the near critical behavior of halogens: thermodynamic and transport properties

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Palavras-Chave: *near critical behavior, halogens, molecular dynamics*

The vicinity of the critical point in the phase diagram is characterized by an anomalous behavior of the physico-chemical properties. Literature presents experimental data which evidence a strong divergence in the thermodynamic properties, such as heat capacities, and transport properties, such as viscosity coefficients and thermal conductivity. [1] The critical point is a singular thermodynamic state which delimits two forms of behavior of real fluid systems in terms of changes of state and marks the end of the liquid-vapor coexistence curve. This state is represented by the critical temperature, pressure and density – T_c , P_c and ρ_c –, i.e. the critical constants. Computational investigations of near critical behavior require the careful use of traditional techniques such as molecular dynamics or Monte Carlo [2,4]. However, to describe with acceptable accuracy the critical divergence of properties, very efficient post-processing techniques must be used to take advantage of the large volume of information generated in molecular simulation. Among them, the estimator MBAR (Multistate Bennett Acceptance Ratio) [4] was especially useful for this purpose [5]. The basis of this technique is the use of simulation data to estimate dimensionless free energies by

$$\hat{f}_i = -\log \sum_{j=1}^K \sum_{g=1}^{G_j} \frac{\exp\{-\beta_i[U_i^{\text{conf}}(x_{jg}) + P_i V]\}}{G_k \exp\{\hat{f}_k - \beta_k[U_k^{\text{conf}}(x_{jg}) + P_k V]\}}$$

With this free energies, values of properties for other thermodynamic states not exploited in simulations can be estimated by

$$\langle \Phi \rangle_i = \sum_{g=1}^G \frac{\Phi(x_g) \exp\{\hat{f}_i - \beta_i[U_i^{\text{conf}}(x_g) + P_i V]\}}{G_k \exp\{\hat{f}_k - \beta_k[U_k^{\text{conf}}(x_g) + P_k V]\}}$$

which is similar to the computation of an ensemble average.

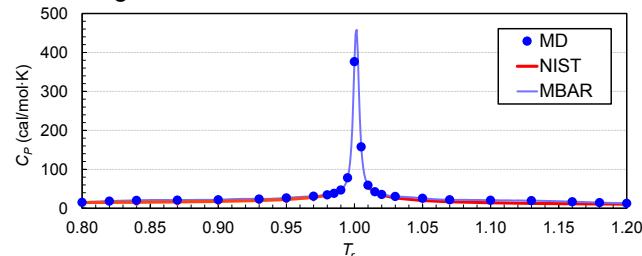
Halogens (F_2 , Cl_2 , Br_2 , I_2) are focused in this work by two reasons. They are important substances for technology and industry applications such as disinfecting of drinking water, production of steel and semiconductor devices [6]. And, because of their reactivity, experimental data for them are scanty or imprecise – especially near the critical point – even in the NIST tables. This investigation presents near critical data of four thermodynamic properties and four transport properties for the halogens mentioned: isothermal compressibility, thermal expansion coefficient, heat capacity at constant volume, heat capacity at constant pressure, self-diffusion coefficient, shear viscosity, bulk viscosity and thermal conductivity.

Method

All molecular simulations were performed with the LAMMPS software. Temperatures and pressures were investigated in the ranges $0,8T_c - 1,2T_c$ and $0,8P_c - 1,2P_c$. The molecules were described by a two-center Lennard-Jones [9] force field and the SHAKE algorithm was used to fix the bond length. The thermodynamic properties were evaluated in the *NPT* ensemble with residual fluctuation formulas similarly to Ref. [6]. The transport properties were evaluated with the Green-Kubo relations following Ref. [3]. The Lennard-Jones parameters – σ and ε – and the bond length ℓ_0 were obtained from [10] and [11]. For all simulations a cut-off radius of 5σ and long-range corrections were used. The post-processing of thermodynamic properties was performed with the software pyMBAR, with $K = 23$ and $G_j = 5000$, while a time decomposition method [12] was used for transport properties with a self-made code.

Results

Our approach has shown to be efficient to compute thermodynamic properties of halogens in the near critical region.



Preliminary results indicate the robustness of the method to describe with good precision the non-anomalous behavior of transport properties.

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Estudo teórico das propriedades espectroscópicas de um complexo dicetonato da família pirazol contendo Eu(III).

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Palavras-Chave: európio, propriedades espectroscópicas, LUMPAC.

INTRODUÇÃO

As dicetonas são ligantes clássicos utilizados em estudos de complexação com vários agentes, em particular, com os lantanídeos. Mas as 1,3-dicetonas da família do pirazol ainda são pouco utilizadas por apresentarem uma baixa disponibilidade e a ausência de um método geral para sua síntese. Neste trabalho foram avaliadas as propriedades espectroscópicas do complexo de Európio (III) [Na(H₂O)[EuL₄].0,0775CH₂Cl₂ (Fig. 1), que foi sintetizado utilizando como ligante a dicetona da família do pirazol 1,3-bis-(1,3-dimetil-1,4-pirazol -4-il)-1,3—propanodiona [1].

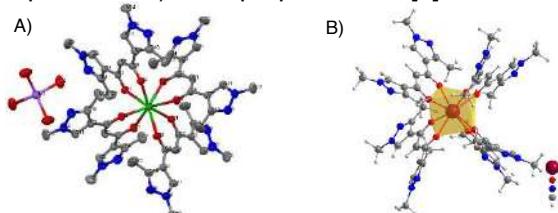


Fig.1. A) estrutura cristalográfica do complexo. B) estrutura molecular otimizada com o modelo PM3/SPARKLE.

RESULTADOS

Todo o estudo teórico foi realizado utilizando o software LUMPAC [2]. A estrutura foi otimizada com o método Sparkle/PM3, foram calculados parâmetros de intensidade (Ω_2 , Ω_4 e Ω_6), taxas de transferência de energia (TE) e taxas de retrotransferência de energia (RTE), taxas de emissão radioativa e não radioativa (A_{rad} e A_{nrad}, respectivamente), eficiência quântica (η) e rendimento quântico (q). Embora Ilja e colaboradores já tenham realizado um estudo experimental desse sistema [1], através dos resultados obtidos foi possível um estudo detalhado do processo de transferência de energia o que possibilitou um melhor entendimento do baixo rendimento quântico de emissão apresentado. Os valores teóricos e experimentais (quando disponível) das propriedades estudadas estão apresentados na Tabela 1.

	EXPERIMENTAL	Sparkle/PM3
Ω_2 (10 ⁻²⁰ cm ²)	8,78	8,60
Ω_4 (10 ⁻²⁰ cm ²)	3,77	3,80
Ω_6 (10 ⁻²⁰ cm ²)	--	0,3668
A _{rad} (s ⁻¹)	429,15	367,26
A _{nrad} (s ⁻¹)	1395,67	1457,56
T(ms)	0,5480	--
η (%)	23,52	20,13
q (%)	--	14,61

Tabela 1: Parâmetros espectroscópicos experimentais e teóricos a partir da estrutura otimizada com o modelo PM3/SPARKLE.

Observando os valores exibidos na Tabela 1, é

possível notar a excelente concordância entre os parâmetros Ω_2 , Ω_4 teórico e experimental. O valor de Ω_2 sugere que existe uma hipersensibilidade na transição $^5D_0 \rightarrow ^7F_2$, indicando a existência de um ambiente químico polarizável ao redor do íon Eu³⁺ devido aos modos de coordenação quelatos do ligante, promovendo uma intensa deslocalização eletrônica de carga. Os valores de A_{rad} e A_{nrad}, bem como da eficiência quântica apresentaram concordância com os resultados experimentais. Os valores de A_{nrad} maiores que os de A_{rad} podem ser causados pela vibração da rede na presença de osciladores, o que acarreta em um *quenching* da luminescência. Na Figura 2 é mostrado um diagrama esquemático que enfatiza os prováveis canais para as taxas de transferência e retro transferência de energia, bem como os valores obtidos para emissão radiativa e não radiativa do sistema de estudo.

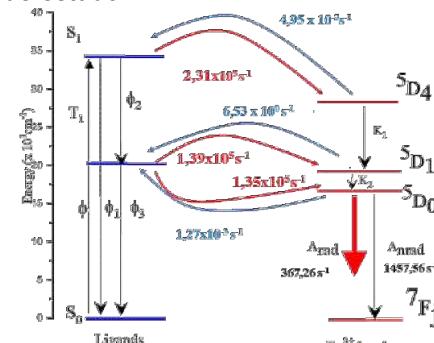


Figura 2: Diagrama esquemático dos prováveis canais de TE e RTE, e valores de emissão radiativa e não radiativa

CONCLUSÃO

Analizando os resultados apresentados podemos concluir que embora os três canais de TE apresentem taxas de mesma magnitude, o processo ocorre com maior contribuição do nível tripleno, uma vez que este transfere para os níveis excitados 5D_1 e 5D_0 , portanto o processo é governado pelo mecanismo de troca. Também foi possível concluir que o baixo rendimento quântico (14,61%) se deve principalmente ao elevado valor da A_{nrad}. No futuro iremos proceder com um estudo sistemático o qual buscará propor modificações na esfera de coordenação desse sistema que o torne mais luminescente.

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“Sandwich” ligand influence on β - and γ -agostic interactions in Pd(II)- α -diimine complexes active in the ethylene polymerization reaction.

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Palavras-Chave: Ethylene polymerization, “Sandwich” ligand, agostic interaction, QTAIM, DFT.

Introduction

Brookhart¹ and co-workers demonstrated in 1995 the catalytic activity on the ethylene polymerization reaction of M(II)- α -Diimines complexes of type ($\text{ArN}=\text{C}(\text{R})=\text{C}(\text{R})=\text{NAr}\text{M}-\text{CH}_3^+$ (with M=Ni, Pd, etc). Several ligands were investigated to improve the catalytic activity of such complexes and modulate the polymer topology. In this way, Brookhart² et. al developed a M(II)- α -Diimines type catalysts with a “sandwich” ligand that produced hyperbranched polyethylene with high molecular weight and low polydispersity index (PDI).³ In order to study the effects of ligand over ethylene polymerization reaction, we performed DFT calculations of first polymerization steps catalyzed by Pd(II)- α -Diimine complex with these ligands that were so-called: “traditional” and “sandwich” ligands (Figure 1).



Figure 1. Pd(II)- α -diimine complexes.

In this study, it was evaluated the sandwich ligand influence over agostic interaction in the ethylene polymerization reaction and its consequences to the polymer topology by AIM analysis.

Computational Details

The complexes' geometries were optimized with B3LYP-D functional and 6-31G(d) basis set for C, H, and N atoms and SDD pseudopotential basis set for Pd. by applying the Gaussian 09 package. The AIM analysis was performed with AIMAll package. The Steric Maps and buried volume (%Vburr) analyses were performed with SambVa⁴. The chemcraft package was used for molecules visualization.

Results

The applied methodology was validated through the calculation of the first ethylene insertion on $\text{CH}_3\text{-Pd}$ bond activation energies. The activation Gibbs free energies calculated were compared with

experimental results: 17.8 kcal/mol for BT-Pd and 19.1 kcal/mol for BS-Pd. The calculated insertion $\Delta G_{\text{theo}}^{\ddagger} = 18.8$ kcal/mol for BT-Pd and $\Delta G_{\text{theo}}^{\ddagger} = 20.1$ kcal/mol for BS-Pd with an error of 1.0 kcal/mol for experimental barriers. Thus, our methodology was considered suitable for this study.

The AIM analysis demonstrate that the sandwich ligand (BS) provides agostic (agt) interactions slightly weaker (BE = -16.35, -28.77 and -27.99 kcal/mol for γ -agt, β -agt and β -agt, respectively) than traditional ligand, BT (BE = -13.81, -28.11 and -27.48 kcal/mol for γ -agt, β -agt and β -agt, respectively). This slight difference is not enough to explain the production of hyperbranched polyethylene by sandwich ligand. Thus, steric maps analysis was performed and showed %Vbur = 49.9 for BS-Pd and %Vbur = 41.0 for BT-Pd indicating that BS-Pd is more hindered and favors the chain propagation and hyper branching.

Conclusions

It was verified that the sandwich ligand saturates electronically the system and, in general, it weakens the agostic interaction. The BS-Pd is more hindered than BT-Pd which favors the chain propagation and may partially justify the high molecular weight of the polymer formed through BS-Pd catalytic systems.

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Propriedades estruturais e eletrônicas de alcanos, alcenos, alcinos, cetonas, aldeídos e ácidos carboxílicos

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Palavras-Chave: funções orgânicas, química quântica, propriedades.

INTRODUÇÃO

A química orgânica se consolidou como uma das grandes áreas da química com diversas aplicações[1]. As várias funções orgânicas possuem diversas características, tanto teóricas quanto experimentais. A química quântica permite uma melhor compreensão de propriedades estruturais e eletrônicas, como energia eletrônica total, energia dos orbitais moleculares, ângulos e distâncias de ligação. A diferença de energia entre os orbitais HOMO e LUMO (*gap* HOMO-LUMO) pode ser relacionada com variados fenômenos. Estudos anteriores relatam que o *gap* HOMO-LUMO de alkanos lineares tende a diminuir com o aumento da quantidade de carbonos e teria correlação com o espectro de absorção [2].

METODOLOGIA

Foram construídos modelos moleculares para: alkanos, alcenos, alcinos, ácidos carboxílicos, aldeídos e cetonas, todas lineares e com número de carbonos variando de 1 à 35. As estruturas foram otimizadas com o método AM1 e as energias obtidas pelo método Hartree-Fock/6-311g+.

RESULTADOS

Todos os cálculos de optimização de geometria convergiram e as energias obedeceram ao teorema do virial. O *gap* HOMO-LUMO diminuiu com o aumento do número de carbonos [3]. Além disso, nota-se que para todos os grupos funcionais estes valores tenderam a uma constante.

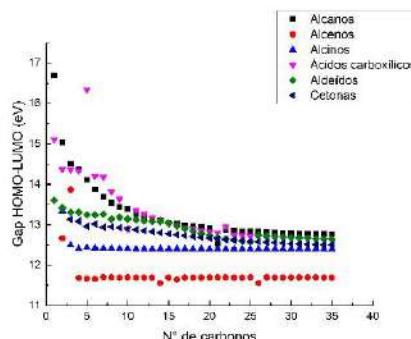


Figura 1: Energia do gap HOMO-LUMO

Para todas as funções orgânicas estudadas a energia do orbital HOMO diminui com o aumento do número de carbonos tendendo a um valor constante. A energia cinética dos orbitais HOMO dos hidrocarbonetos também aumentam com o número de carbonos indo para um valor constante. A energia do LUMO se mantém praticamente constante. Para

os ácidos carboxílicos, aldeídos e cetonas, a energia cinética dos orbitais HOMO diminui com o aumento do número de carbonos tendendo a um valor.

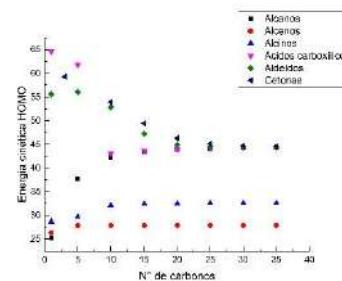


Figura 2: Energia cinética dos orbitais HOMO

O *gap* HOMO-LUMO distingue os alcenos e alcinos tanto pelo comportamento constante quanto pelos valores em si. Percebemos uma ordem de diminuição geral na sequência: alkanos, ácidos carboxílicos, aldeídos, alcinos e alcenos.

Para todos os grupos funcionais as distâncias e ângulos de ligação não tiveram mudanças significativas.

CONCLUSÕES

Foi possível diferenciar os hidrocarbonetos dos grupos carbonilados devido ao comportamento inverso da energia cinética do elétron do HOMO com o aumento do número de carbonos da cadeia. O *gap* HOMO-LUMO distingue claramente os alcenos e alcinos das demais funções. O comportamento nas cetonas e aldeídos, embora similares, apresentam valores diferentes. A partir de 25 carbonos os valores para os aldeídos e ácidos carboxílicos são praticamente iguais.

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DFT study of the dichloro(L-histidine) copper(II) coordination complex

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Keywords: Coordination complex, DFT, Amino acid.

INTRODUCTION

Amino acids are biomolecules with important functions. Ions formed from these compounds can also constitute coordination complexes, with the formation of bonds between their N and O atoms and transition metals. In this way, the study of interactions at the molecular level of complexes formed with amino acids and divalent metals have drawn the attention of researchers, as they have considerable properties in biological systems, related to the nature of bonds and the pattern of coordination to the metal.¹ Thus, the present work aims to study structural, electronic and thermodynamic properties of the dichloro(L-histidine)copper(II) complex.

METHODS

Computational calculations were performed using the Gaussian16² software, employing the DFT functional B3LYP with the 6-311++G(d,p) basis set for H, N, C and O atoms, and the Stuttgart-Dresden (SDD) basis sets, and pseudo-potential for Cu²⁺. The solvation effects was included with the IEFPCM method, using methanol as a solvent. The results were analyzed using the Chemcraft graphical interface software.

RESULTS

The electrostatic potential map, frontier molecular orbitals and thermodynamic properties were obtained from the optimized geometries, for which all vibrational frequencies are positive. The geometry of the complex is square planar, with the amino nitrogen and carboxyl oxygen of histidine bonded to the copper atom. Comparison with experimental parameters shows a correlation factor of 0.9860 Å and 0.9498 Å, respectively. The electrostatic potential map (Fig. 1) shows the main regions favorable for nucleophilic and electrophilic attacks.

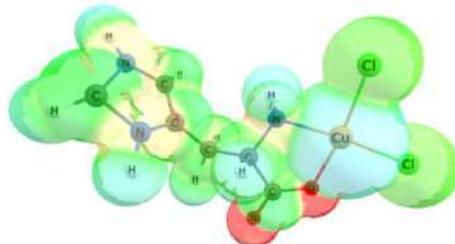


Figure 1 - Electrostatic potential map of the coordination complex

HOMO and LUMO orbitals were also studied, with calculated energy values of -5.427 and -1.340 eV, respectively. From the frontier molecular orbital energies, additional reactivity indexes were computed. The values of the Gibbs free energy and enthalpy changes associated with the coordination of dichloro(L-histidine) to copper(II) were obtained through Equations 1 and 2, as shown below. The results are $\Delta G = -277.92$ and $\Delta H = -301.63$ kcal/mol.

$$\Delta G = G_{\text{complex}} - (G_{\text{histidine}} + 2 \cdot G_{\text{Cl}} + G_{\text{Cu}}) \quad (1)$$

$$\Delta H = H_{\text{complex}} - (H_{\text{histidine}} + 2 \cdot H_{\text{Cl}} + H_{\text{Cu}}) \quad (2)$$

CONCLUSION

Several properties of the complex were calculated from the theoretical study, contributing to the characterization of the materials and confirming the spontaneity of the coordination of dichloro(L-histidine) to copper(II).

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Confinamento eletrônico em moléculas e nanoestruturas

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Palavras-Chave: Confinamento eletrônico, moléculas, nanoestruturas.

INTRODUÇÃO

O confinamento eletrônico em moléculas e nanoestruturas permite estudos preliminares para futuros dispositivos mais sofisticados¹. Na abordagem intrínseca unidimensional, o hamiltoniano tem apenas o termo cinético. Em uma abordagem extrínseca² além do termo cinético surge um termo de potencial geométrico (V_{geo})³. Ainda não se sabe ao certo qual abordagem deve ou pode ser adotada para sistemas quânticos. Cálculos Hartree-Fock em modelos moleculares podem ser comparados com modelos de confinamento do tipo Da Costa a fim de entender melhor sua necessidade.

METODOLOGIA

A equação de Schrödinger unidimensional para o confinamento do tipo Da Costa apresenta a seguinte forma:

$$\frac{d^2}{ds^2} \Psi(s) = \left(-\frac{\hbar^2 k(s)^2}{2\mu} - \frac{E^2 \mu}{\hbar^2} \right) \Psi(s) \quad (1)$$

Onde, s é o comprimento de arco, $k(s)$ é a curvatura da curva, μ é a massa da partícula e $\hbar^2 k(s)^2 / 8\mu$ é o potencial geométrico (sempre atrativo). Modelos moleculares com apenas um elétron, utilizando átomos fantasmas, podem ser calculados usando o método Hartree-Fock/6-311+G(d).

RESULTADOS

Para os sistemas lineares o elétron se localizou numa região de comprimento de 13,9 Å, -0,5 de carga (Fig. 1), independentemente do número de centros do modelo molecular, mantendo praticamente a energia constante igual a 1,0791 eV.

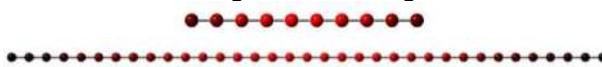


Figura 1: Distribuição de carga do elétron no confinamento linear.

O modelo analítico prevê a energia de 0,6331 eV na região de maior densidade de carga. Supondo a região de cargas localizadas via método HF, temos uma concordância com os modelos. No caso do círculo o elétron está deslocalizado igualmente e a energia fica em torno de 1 eV. Nos sistemas cúbicos a densidade eletrônica se localizou entre as regiões de maior curvatura (Fig. 2). Considerando essa região de 5 centros o elétron teria a energia 0,98 eV segundo o modelo de confinamento. Os cálculos HF mostram que a energia desse sistema se mantém próximo ao valor de 0,94 eV independentemente do tamanho da cúbica.

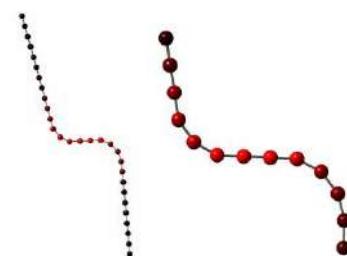


Figura 2: Distribuição de carga do elétron no confinamento de cubicas.

Nos sistemas parabólicos o elétron se localizou na região de maior curvatura, correspondendo a distribuição de carga no comprimento de 16,94 Å (Fig. 3). A energia permaneceu próxima de 1,0235 eV a partir de 20 centros. Considerando 7 centros localizando o elétron, a energia no modelo intrínseco seria 0,4396 eV. Este valor embora menor que o obtido computacionalmente é maior que o previsto por Da Costa.



Figura 3: Distribuição de carga do elétron no confinamento de parabolás.

A energia do elétron nas parábolas não muda tanto em relação aos sistemas lineares, porém diminuem com o aumento da curvatura e sua carga se concentra mais. Este comportamento é previsto pelo modelo de Da Costa.

CONCLUSÕES

A energia do elétron e sua localização variam com o aumento da curvatura das curvas de confinamento. Este comportamento concorda com o modelo de Da Costa. A densidade eletrônica e a energia variam pouco com o aumento do número de centros (tamanho da região de confinamento). Buscaremos ampliar este estudo para sistemas bidimensionais.

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AGRADECIMENTOS





Exploration of copper bimetallic alloys for modulating CO adsorption using alchemical derivatives

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Keywords: *Alchemical Transmutations, CO₂ER, Catalysis.*

The amount of CO₂ concentration in Earth's atmosphere has been surging for the past few years. To mitigate the damaging effects caused by this Greenhouse gas, a myriad of research has been conducted to develop catalysts to ease CO₂ electrochemical reduction to high-value products. The most appealing pure transition metal for this reaction is Cu. However, large external potentials are required, besides its low selectivity. It is well-established that the high overpotential in CO₂ER is associated with the *CO hydrogenation to *CHO/*COH and that this step has a key role in the selectivity towards methane, methanol, or C₂ products.

Inasmuch as CO adsorption is involved in the rate-determining step of CO₂ER, we have investigated CO adsorption on Cu-based alloys using computational alchemy. Currently, the most used method in computational chemistry for large systems is the density functional theory (DFT). Nevertheless, DFT is still computationally expensive, which can hamper new approaches to quickly search through the chemical space, and then act as a constraint to inverse design or high throughput procedures. A promising alternative to standard DFT calculations is alchemical transformations. In this approach, one can compute hypothetical alloys structures and adsorption energies in a manner a thousand times faster than expected with DFT. This allows for more alloy configurations that can be screened to determine the ideal metal composition for CO-metal interactions to be used in CO₂ER applications.

In this work, we have used alchemical derivatives for the chemical space exploration of copper bimetallic alloys with Zinc and Gold. Starting from pristine metals slabs, the effect of changing single atoms on CO adsorption energies was computed using both alchemical derivatives and delta SCF calculations. We have also investigated whether the effect of single substitutions could be used for predicting the effect of multiple site substitutions. Moreover, we explored the impact of geometry relaxation in affecting the predictive power of alchemical derivatives.

DFT study of structure and electronic properties of dapsone and its interactions with oxalic acid in the formation of the amorphous material

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Keywords: DFT, dapsone, leprosy

INTRODUCTION

Dapsone¹ is an oral antibiotic used to treat diseases such as tuberculosis and leprosy. It belongs to the Class 2 of the Biopharmaceutical Classification System due to its low water solubility. Thus, like reported in other studies, the preparation of solid dispersions of drugs is a viable alternative to increase their solubility, which can help to improve the therapeutic effectiveness of dapsone. Since theoretical methods are valuable for the study of chemical systems, ions formed from the drug dapsone and the coformer oxalic acid, as well as their interactions, were studied by means of DFT calculations². The study allows the determination of properties of these systems, contributing to a better understanding of the formation and stability of the formed solid dispersion.

METHODS

The *Chemcraft* software was used to build the chemical structures for the preparation of the input files for the computational calculations and also for the analysis of the results. The DFT² functional ω B97x-D³ was used in association with the basis set 6-311++G(d,p) for the development of the calculations, with the solvation effects study developed with the IEFPCM method, using methanol solvent, as implemented in *Gaussian16* software. Geometry optimization calculations were performed for each ion individually, and the starting geometries for the interactions calculations were built from the optimized geometries of the ions, with the ionic interaction sites with higher affinity being closer to each other. Vibrational frequencies calculations were developed after each geometry optimization.

RESULTS

Spectroscopic and thermodynamical data, partial atomic charges, electrostatic potential maps, dipole moment, spacial distribution and energies of molecular orbitals were obtained from the optimized geometries calculated. The starting geometries used in the calculations performed for the interaction study were designed based on the parameters determined for the individual compounds, and the optimized geometry for the system involving an important drug-coformer interaction was obtained, as presented in Figure 1.

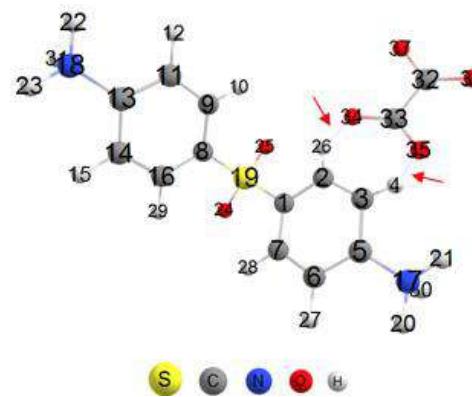


Figure 1. Geometry optimized of the system with dapsone interacting with the coformer

As it can be seen, a possible intermolecular interaction is occurring between atoms 34 and 35 of oxalate ion with atoms 26 and 4 of protonated dapsone, respectively. The interaction free energy value calculated is -2,263 kcal/mol, and the basis set superposition error value calculated is 1,223 kcal/mol.

CONCLUSIONS

DFT calculations were developed for the study of the compounds and their ions individually, contributing for the characterization and better comprehension of the properties of these classes of compounds. Based on the thermodynamical parameters determined, it was observed that the variation of Gibbs energy associated with the interaction studied is negative, confirming it is spontaneous, contributing to the formation of the material.

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The Effect of Positional Disorder on Charge Survival Probability in Organic Semiconductors: A KMC Analysis

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Keywords: *Organic Semiconductors, Exciton Generation, Charge Recombination, KMC Simulations.*

Abstract

Organic photovoltaics (OPVs) efficiency has increased slowly over the past three decades and is still far from rival the inorganic counterparts. Some OPVs properties, such as low cost, flexibility, lightness and transparency, still push research and academia in the direction of improving conversion efficiency.

Computer simulations can enormously improve this class of devices: design of new acceptor/donor materials, the impact of dopants, domain sizes, etc., are tested even before they need to be manufactured, reducing significantly the time that materials' engineers need to design new devices.

However, many algorithms used to simulate exciton and charge dynamics have not yet implemented the Beer-Lambert law of attenuation of radiation absorption and simply use a random pattern to generate excitons.

As pointed out by Lunt and co-workers,[1] this work has incorporated into the simulation a generation rate, $G(x)$, with the following expression:

$$G(x) = \frac{\Phi_{photo}}{\cos(\theta_\lambda)} \exp\left(-\frac{\alpha x}{\cos(\theta_\lambda)}\right)$$

where Φ_{photo} is the flux of incident photons, α is the absorption coefficient, which is related to absorbance by $\sigma = \alpha/N$, where N is the number of basic constituents of the material (chromophores or whole molecules, for example) per unit volume, and θ_λ is the angle of incidence at the surface which already takes into account the refraction in higher layers, whether these layers are passivation layers, electrodes, or filters.

Including this mechanism in the simulation, we obtained internal quantum efficiency curves as a function of the thickness of the semiconductor film. And these curves are in better agreement with analytical expressions when compared to the agreement of the experimental.[1]

With excitons generated in more realistic positions, we proceeded with the simulation, turning our attention to charge diffusion, in order to improve previous studies.[2] Our results show that the conversion of light energy into free charge approaches 100%.

Once at the interface, with the correct bandgap, we have that electron and hole will become weakly bounded, constituting what we call a charge-transfer exciton.

This exciton, in turn, can be dissociated generating charges through several mechanisms, such as Energy Bending (EB). These mechanisms can yield an internal efficiency of light energy conversion into free charge approaching 100%.

The loss of efficiency begins to occur with the diffusion of these charges towards the electrodes, as non-geminated recombination processes can happen along the way.

In order to investigate this aspect in a system that is equivalent to a small region of a bulk heterojunction, we analyzed, for different intensities of EB, the positional disorder as a function of the donor's domain size.

In this configuration, we could observe that, without EB, the positional disorder can raise the Charge Survival Probability (CSP) to, at most, 30%.

As the EB increases, the growth of the positional disorder starts to have a more significant influence on the raise of the CSP.

Nevertheless, we have shown previously,[2] EB alone is able to raise the CSP to almost 80%, when it is set at 0.5 eV. For the same EB value, the maximum positional disorder considered here (10^{-10} m) raised the CSP to 95%.

Our simulations suggest that the positional disorder of typical polymers, when reproduced in the simulation, is revealed as a CSP increase factor, but a minor one. Besides, we also concluded that ordered domains can contribute more significantly to increasing the external efficiency of organic photovoltaic devices.

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Existência de Moléculas Diatômicas e Triatômicas em Manchas Solares

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Palavras-Chave: Moléculas lineares; Manchas solares; espectroscopia;

INTRODUÇÃO

Ainda não se sabe ao certo a composição das manchas solares, quais moléculas estão presentes e que consequências podem causar. Polyansky^[1] identificou a presença de moléculas de água nas manchas solares a partir da comparação do espectro de infravermelho obtido a altas temperaturas e os espectros experimentais do Sol^[2]. Outras moléculas foram estudadas em relação a sua presença no Sol: CO₂, HCN, SiO e HF^[3]. Algumas destas moléculas podem ter relação com características das manchas solares, como o fato de sua temperatura ser menor que no restante do Sol e seu campo magnético ser maior. Leite et. al identificou 67 transições rotovibacionais na região entre 537 cm⁻¹ a 925cm da molécula de água no primeiro estado eletrônico excitado, nos espetros experimentais das manchas solares. A molécula de água neste estado eletrônico apresenta momento magnético que pode estar influenciando no campo magnético das manchas solares.

Neste trabalho estudamos a existência nas manchas solares das seguintes moléculas no estado eletrônico fundamental: HCN, NNO, NO⁻, HF, HCl ,CO, OCS, C²⁻, H₂⁺ e N₂⁺.

METODOLOGIA

O espectro rotovibacional de moléculas diatômicas pode ser obtido pela seguinte equação:

$$E = B_e J(J+1) - D_e J^2(J+1)^2 + W_e \left(\frac{1}{2} v\right) W_{eXe} \left(\frac{1}{2} v\right)^2 - \alpha_e \left(\frac{1}{2} v\right) J(J+1) \quad (1)$$

Onde W_e é a constante da contribuição anarmônica $B_e J$ é a constante do Rotor Rígido, J é o número quântico rotacional, α_e a contribuição de Coriolis. As moléculas triatômicas são obtidas pela equação:

$$E = v_2 \left(\frac{1}{2} + n_1 + \frac{1}{2} + n_2 \right) + v_1 \left(\frac{1}{2} + n_3 \right) + v_3 \left(\frac{1}{2} + n_4 \right) W_{eXe} \left(\frac{1}{2} + n_3 \right)^2 + B_e J(J+1) - D_e J^2(J+1)^2 - \alpha_e \left(\frac{1}{2} + n_3 \right) J(J+1) \quad (2)$$

Onde v_1 , v_2 , v_3 são respectivamente as freqüências simétrica, flexão (tesoura) e antissimétrica, n_1 e n_2 são os números quânticos de tesoura e n_3 e n_4 pertencem aos números quânticos simétricos e assimétricos. A partir dessas equações é possível comparar transições rotovibacionais com o espectro infravermelho das manchas solares^[3].

RESULTADOS

Foi analisada a faixa do espectro de infravermelho de 473 cm⁻¹ – 925 cm⁻¹.

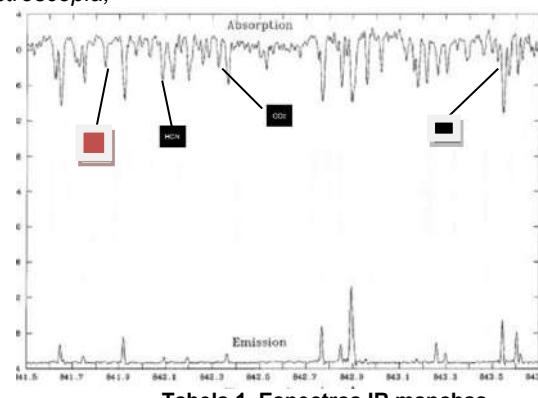


Tabela 1. Espectros IR manchas

A quantidade de picos encontrados J=1 a 50 para as moléculas de HCl, HF, CO, NO⁻, H₂⁺, N₂⁺, C₂⁺, OCS, NNO, HCN foram respectivamente 19, 34, 24, 22, 15, 9, 12, 40, 35, 29. Este resultado indica a presença mais provável de: OCS e NNO nas manchas solares. A molécula de NNO é paramagnética e pode estar contribuindo para o maior campo magnético nas manchas solares em relação ao Sol, assim como as possíveis de água descritas por Leite et. al^[2].

CONCLUSÃO

A partir do cálculo das transições rotovibacionais e da comparação com o espectro infravermelho experimental das manchas solares, identificamos a provável existência das moléculas OCS e NNO no Sol, esta última podendo contribuir para o campo magnético das manchas solares.

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AGRADECIMENTOS

Um agradecimento a todos os meus amigos do laboratório e em especial ao meu orientador Prof. Dr.Cristiano Bastos.



Formação de fluoreto de hidrogênio (HF) e seu cátion a partir da fotólise de $\text{CF}_3\text{CH}_2\text{F}$: investigações cinéticas e termodinâmicas

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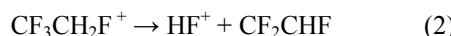
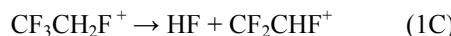
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Palavras-Chave: HFC-134a, teoria do estado de transição, DFT.

Introdução

Uma molécula com dois átomos do mesmo elemento em ambientes químicos distintos serve como um bom sistema-teste para avaliar fragmentações sítio-específicas. Nesse contexto, pode-se dar uma especial importância à molécula 1,1,1,2-tetrafluoroetano ($\text{CF}_3\text{CH}_2\text{F}$, ou HFC-134a ou mesmo R-134a), que tem sido objeto de diversos estudos.¹⁻⁴ Além disso, essa molécula tem recebido atenção devido à sua vida atmosférica de 14 anos, ainda que menos agressiva ao meio ambiente que compostos análogos sem hidrogênio.² Conforme relatado por Pereira-da-Silva et al.,⁴ um dos produtos da decomposição de R-134a são a molécula HF ou seu cátion HF^+ . A cinética de formação desses compostos a partir de $\text{CF}_3\text{CH}_2\text{F}$ foi investigada apenas experimentalmente, a altas temperaturas.⁵ Neste trabalho procuramos preencher essa lacuna na descrição de processos de recombinação decorrentes da fotólise de R-134a.

Metodologia

Até o momento, estudamos neste trabalho as rotas:



Todas as espécies químicas têm as geometrias de equilíbrio totalmente otimizadas sem qualquer restrição geométrica. Essas geometrias são avaliadas via análise das frequências vibracionais harmônicas, sem fatores de correção. Na otimização das geometrias é utilizada a teoria do funcional de densidade (DFT) na forma M06-2X, e conjunto de funções de base – ou base – de Dunning denominado cc-pVTZ. Para obter parâmetros cinéticos de boa qualidade, todos os resultados em energia são ainda refinados via método Coupled Cluster com excitações simples, duplas e tratamento quasi-perturbativo de excitações triplas conectadas – CCSD(T), considerando a base de Dunning do tipo cc-pVXZ ($X=Q, 5$), e os valores energéticos são extrapolados para o limite da base completa. As barreiras de ativação assim obtidas são então usadas no cálculo de coeficientes de velocidade k das reações

correspondentes. Realizamos os cálculos de estrutura eletrônica no pacote Gaussian 16 e os de caráter cinético no Multiwell 2017.

Resultados

Atestando a qualidade dos resultados do funcional M06-2X, a energia de ionização adiabática para $\text{CF}_3\text{CH}_2\text{F}$ no nível M06-2X/cc-pVTZ é de 12,08 eV, apenas 0,17 eV abaixo dos resultados já refinados via “G2” de Zhou et al.,³ e por volta de 0,5 eV abaixo do valor experimental dos mesmos autores.

A Figura 1 apresenta a barreira de ativação de 29,40 kcal/mol da reação (1C), bem menor do que a barreira da reação de (1N), 78,90 kcal/mol. Apesar disso, a ΔE da soma de (1) com (1C) ainda é ~ 10 vezes maior que a barreira de (1N). Já (2), tem ΔE ainda maior, de 123,8 kcal/mol.

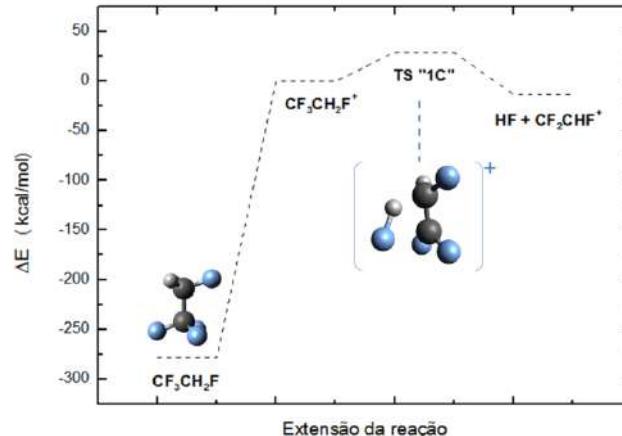


Figura 1: Representação simplificada de um dos caminhos de formação de HF a partir de $\text{CF}_3\text{CH}_2\text{F}$, em nível M06-2X/cc-pVTZ, destacando o TS “1C”.

Conclusões

Os resultados preliminares sugerem que a formação de HF (e CF_2CHF^+) é mais favorável que a de HF^+ .

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DFT study of rifampicin and its interaction with tromethamine in the formation of an amorphous material

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Keywords: DFT, rifampicin, tromethamine

INTRODUCTION

Density Functional Theory (DFT)¹ has been used intensively to determinate properties of the ground state of multielectronic systems, considering electronic density as a fundamental parameter, like drugs used in medicine. Rifampicin is a drug used to treat leprosy and tuberculosis, since it inhibits the multiplication of bacteria². Tromethamine has a chemical structure constituted by polar groups, with high affinity to water molecules, which justify its high water solubility. In this way, tromethamine has been used as a coformer in the preparation of solid dispersions in recent years, enabling the modulation of physicochemical properties of drugs poorly water-soluble drugs. Consequently, it is possible to increase the dissolution rate of drugs in water, and also their bioavailability³. In this work we performed a theoretical study of rifampicin and of its interaction with TRIS, through the use of the DFT functional ω B97x-D in association with the basis set 6-311++G(d,p), as implemented in Gaussian 16 software.

METHODS

The representations of the chemical structures of the compounds were obtained from a crystallographic database, and treated using the software Avogadro, for the preparation of input files. The calculations were then submitted to a cluster of high performance computers, and were developed by using the DFT functional ω B97x-D, and the basis set 6-311++G(d,p). The solvation effects were studied by using the IEFPCM method. The optimized geometry for each compound was obtained individually firstly, and then the interactions RIF-TRIS were studied. Vibrational frequencies were calculated after each geometry optimization calculation.

RESULTS

Structural, electronic and thermodynamic properties of the compounds were calculated. Spectroscopic data was obtained, contributing to the characterization of the systems, and the drug-coformer interactions were studied. Thermodynamical data obtained confirm that the intermolecular forces between the compounds are contributing to stabilize the material formed. The calculated Gibbs free energy variation associated with the interaction is equal to -4,647 kcal/mol and the

basis set superposition error calculated value is 0,008 kcal/mol. A favourable interaction found is represented in Fig. 1, shown below.

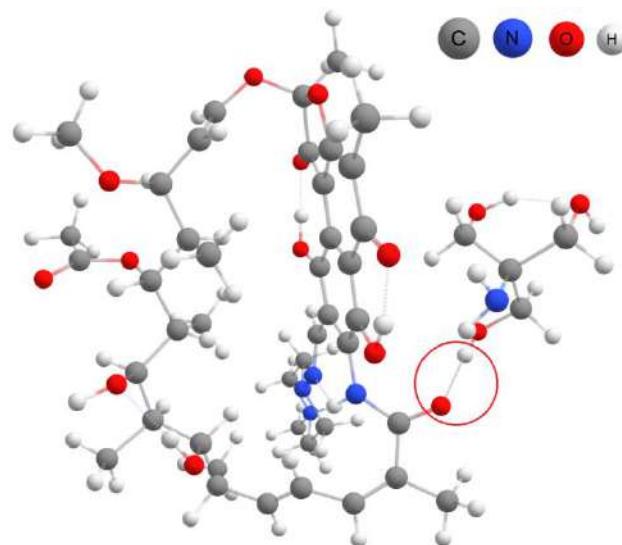


Figure 1. Most stable rifampicin-tromethamine interaction

As it can be seen from the picture, the interactions between the compounds occur with the formation of hydrogen a bond between the molecules, contributing to the stability of the material.

CONCLUSIONS

From the study it was possible to calculate several properties of the compounds, and also to study their interactions. The results confirm the contributions of the interactions to the stability of the material formed, and also contribute to the characterization of the materials.

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Substituent Effects on the Structure and Aromaticity of Benzene Derivatives: Special Cases

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Keywords: substituent effects, aromaticity indices, multireference methods.

Introduction

Over the years, substituent effects have been extensively investigated in various classes of molecules, both experimentally and theoretically. Such studies have, for example, motivated thermodynamic and kinetic stabilization strategies in various materials, since the incorporation of different substituents allows the adjustment of their properties and consequent extension of the range of possible applications. The effect of substitution(s) on the structure and properties — in particular the aromaticity — of benzene is one of the subjects that has especially attracted the attention of researchers.¹ It was found that the substituents attached to benzene influence only very weakly the π -electron delocalization in the ring, and the changes in aromaticity indices are almost negligible. However, special cases were found in which the disturbance due to the substituent on the π -electron structure of the ring is substantial.^{1,2} The purpose of this study is to analyze the consequences of the substituent effect on π -electron delocalization in these special cases.

Methodology

In this study, the effects of substituents on π -electron delocalization of benzene were probed through structural (HOMA), vibrational (Al(vib)), magnetic (NICS), and electron localization function (ELF) indices. The singlet-triplet splitting has been investigated based on the high-level multireference configuration interaction MRCI method, which also provided rigorous information on the electronic structures.

Results

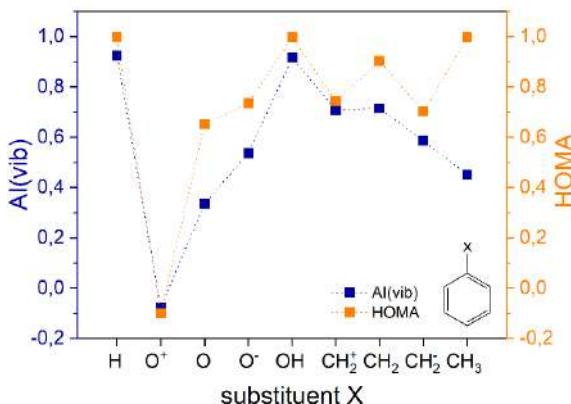


Figure 1. HOMA and Al(vib) indices for benzene and monosubstituted benzene derivatives. Values close to 1 indicate greater aromaticity. B3LYP/def2TZVP calculations.

Figure 1 presents the indices of aromaticity HOMA and Al(vib) for benzene and monosubstituted benzene derivatives. The indices point to lower aromaticity for the structures with the substituents O⁺, O, O⁻, CH₂⁺, CH₂, and CH₂⁻. Similar results were obtained by the NICS index. Topological analysis of the π component of the electron localization function (ELF _{π}) shows that, in these cases, there is a strong interaction between the substituent and the π -electron system of the ring.

Figure 2 shows the cases with CH₂⁺ and CH₂⁻ substituents, in which the empty 2p_z orbital of the CH₂⁺ substituent interacts with the π -electron moiety of the ring and the 2p_z electron pair in the CH₂⁻ substituent with the π -electron system of the ring. On the other hand, the systems with groups OH and CH₃ present indices with values close to those observed for benzene. As expected, these results are in perfect accordance with the singlet-triplet splitting results based on the MRCI method.

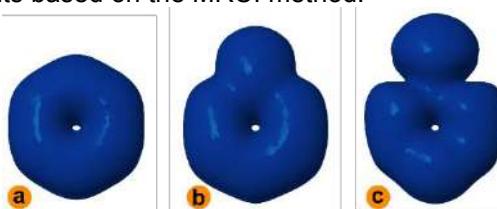


Figure 2. ELF _{π} isosurface of benzene and monosubstituted benzene derivatives. a) X=H, b) X=CH₂⁺, c) X=CH₂⁻.

Conclusions

The present investigation provides a detailed theoretical contribution to elucidating the effect of substituents on the π -electron delocalization of benzene. In general, if the substituent has orbitals of suitable size and symmetry available for mixing with the π -orbitals of the benzene ring, the contributions from the polar canonical forms increase and account for the changes observed.

Acknowledgments

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Teoria do Funcional de Densidade (DFT) aplicado ao estudo das interações eletrostáticas entre a dopamina e a glucosamina

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Palavras-Chave: Dopamina, Glucosamina, Teoria do Funcional de Densidade.

INTRODUÇÃO

A dopamina é um neurotransmissor essencial para o corpo humano, uma vez que contribui para atividades como comportamento, memória, movimento, sono e cognição¹. Atualmente, diversos trabalhos têm unido esforços para melhorar a entrega cerebral desse neurotransmissor, a fim de otimizar tratamento de doenças como o Alzheimer² e também obter processos cada vez mais precisos e exatos para detectar o nível de dopamina no sangue³. Também, a quitosana, um biopolímero com propriedades biocompatíveis e atóxicas ao corpo humano⁴, tem sido alvo de estudos junto a dopamina com a finalidade de otimizar tarefas⁵. Visto a importância de estudos que envolvam a pesquisa a favor desse neurotransmissor, esse trabalho pretende investigar as interações entre a dopamina e a glucosamina (monômero da quitosana) via nível de teoria DFT.

METODOLOGIA

Foram realizados cálculos computacionais para observar a conformação geométrica do sistema e as interações não-covalentes. A análise conformacional foi realizada com o software GFN2-xTB e os cálculos de otimização geométrica e single point foram feitos com o software ORCA 4.2.1, na qual foram empregados o funcional wB97X-D3, função de base def2-SVP e função de base auxiliar def2/J.

RESULTADOS

A otimização geométrica do sistema mostra como que a dopamina e a glucosamina se arranjam no espaço e interagem, conforme mostra a Figura 1:

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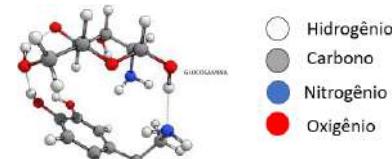


Figura 1 - Sistema com geometria otimizada

O mapa de interações não-covalentes foi plotado com o auxílio do software Jmol, onde na Figura 2 nos mostra como que o sistema interage eletrostaticamente. Pode-se perceber que a dopamina e a glucosamina realizam em dois locais diferentes, interações de forças atrativas (ligações de hidrogênio) nas extremidades de suas moléculas, enquanto que no centro do sistema dominam as interações de Van Der Waals. Forças repulsivas estão presentes principalmente no centro de cada molécula.

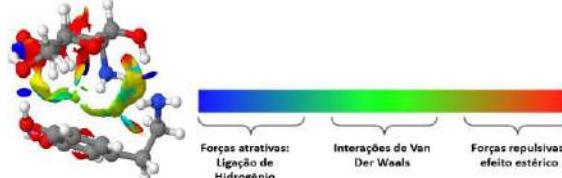


Figura 2 - Mapa de Interações Não-Covalentes

CONCLUSÃO

Visualmente, é possível observar que o sistema possui fortes interações, o que justifica o mesmo estar sendo amplamente estudado. Mais estudos envolvendo características como as propriedades eletrônicas do sistema são recomendados, junto com a união de outras espécies químicas que possam auxiliar nos processos almejados. Esse trabalho encontra-se em andamento.



How Julia Language can speed up electronic structure calculations? A Hartree-Fock benchmarking

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Keywords: Julia Language, Python, Benchmarking, Hartree-Fock

Introduction

Nowadays, scientific computing is standing right to the next level of influence in knowledge discovery, aiming new theoretical analysis and time gain improving, accelerating the finding of new results in Chemistry, Biology, Physics, and Mathematics. In the last ten years, new programming languages have been emerged, such as Julia, to improve scientific computation with better numerical programming tools and Machine Learning features. A programming language is a formal code of communication that contains a set of instructions to generate series of computer outputs through the implementation of algorithms, that is, some of them are mainly declarative (which specifies the results to be achieved) or imperative (which defines sequences of operations to perform). In terms of performance, programming languages can be divided into three major groups: (I) low level: close to machine language (assembly), having high performance, but difficult to implement due to the degree of complexity; (ii) high level: longer code compilation time, low performance, but easy implementation due to the greater similarity with the language of human understanding; (iii) mixed: tries to mix the best of both worlds to minimize disadvantages and optimize usage¹.

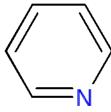
Methodology

The Hartree-Fock STO-3G² benchmarking had been performed in Python and Julia Language using BenchmarkTools package, comparing the molecular energies and total execution time with ORCA program calculations in serial execution(using a intel core i5 processor-10 generation- H series). With Julia Language code, the LinearAlgebra package had been used to provide matricial equations resolutions, and with Python code, Numpy³ had been applied.

Results and Discussion

The Hartree-Fock⁴ calculations performed are described in Table 1, showing that Julia is so much faster than Python. The values in relation to ORCA results were numerically approximated, representing the quality of employed calculations to more than 30 molecules studied.

Table 1. Results from benchmarking, comparing electronic energies reported in Hartree/(Eh) and total execution time/(s). The ORCA software obtained results are the reference used for further comparisons.

Molecule	Total Execution Time		
	Julia	Python	ORCA
H ₂ O	-75.16 Eh 8.712 s	-75.21 Eh 89.833 s	-74.97 Eh 3.869 s
NH ₃	-55.89 Eh 9.104 s	-56.009 Eh 98.007 s	-55.45 Eh 3.707 s
CH ₄	-39.99 Eh 7.930 s	-40.09 Eh 83.967 s	-39.73 Eh 2.220 s
Cl-CH ₃	-493.85 Eh 20.564 s	-493.89 Eh 101.86 s	-493.72 Eh 6.552 s
	-228.03 Eh 24.988 s	-228.18 Eh 115.98 s	-227.89 Eh 7.760 s
	-243.75 Eh 30.723 s	-244.00 Eh 140.14 s	-243.64 Eh 8.895 s

Conclusion

The Hartree-Fock solution was verified in comparison with the results obtained by the ORCA software. In addition, the home-made programs took more time than the used reference, as pointed in Table 1.

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Exploring Reactive Sites of Textile Dyes

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Keywords: *Textile Dyes, DFT, Molecular Dynamics.*

Introduction

The Brazilian Northeast is marked by water scarcity. Of all the freshwater available globally, only 3% is in this region, with a critical water availability of less than 1500m / inhab / year. These factors contribute to a difficulty in accumulating surface water, as rivers and streams in the region are intermittent, such as the Capibaribe River. The textile segment for the Agreste of Pernambuco represents economic development for the region and is relevant in terms of employment and production, with agglomerations of this type of industry. In addition, however, the sector contributes to improving the environment, with the discharge of its effluents that are highly contaminated in water bodies and the terrestrial environment. Dyeing is one of the main processes for the textile industry due to the great demand for products with color diversification, or that justifies a wide variety of available and used dyes. This work's goal was to analyze structural and reactivity aspects of the significant dyes used in the region: acid red 88 and direct black 88.

Methodology

The dyes structures were optimized at the density functional theory level using the exchange-correlation functional BP86 and the set of base functions cc-pVDZ. Solvent effects were treated using the Continuous Polarizable Model (PCM). With the optimized geometries, a search for reactive sites on the dyes molecules was carried according the CDFT formalism. From the previous optimized geometries, a conformational analyzes in solution were performed through molecular dynamics simulations.

Results

The mapping of the electrostatic potential of dye molecules, figure 1, was carried out to assess how the charge distribution is spread across the molecule and thus characterize regions with a higher concentration of negative and positive charges.

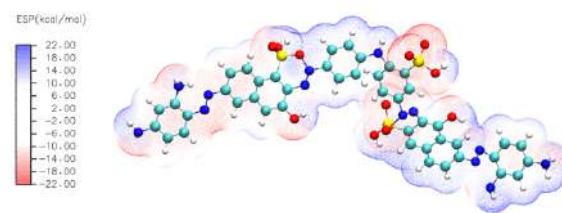


Figure 1 Optimized structure of dye molecules: (top) Acid Red 88 and (bottom) Direct Black 88 and their respective calculated electrostatic potential surface maps.

Figure 2 shows the map of the calculated dual function of the dyes. In green, the regions dominated by positive values of $\Delta f_w(r)$ are shown, which characterizes reactive sites more favorable to suffer nucleophilic attacks. In pink, the regions dominated by negative values of $\Delta f_w(r)$ are shown, which characterize regions of the molecule more susceptible to electrophilic attacks.

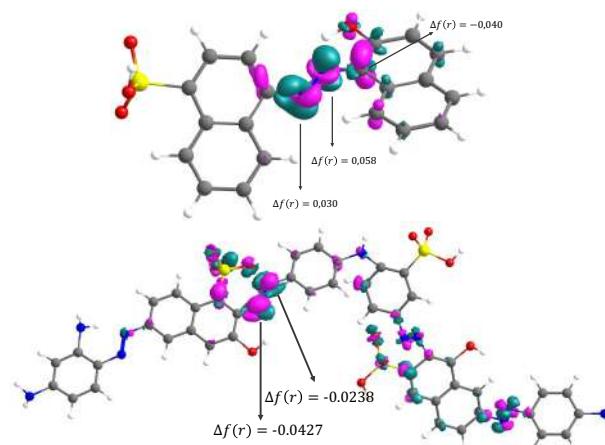
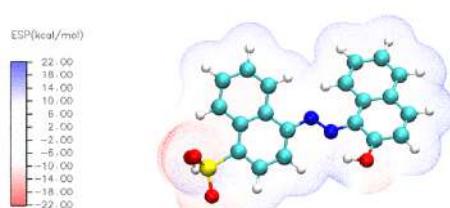


Figure 2 - Map of the dual function $\Delta f_w(r)$ calculated for: (top) Acid Red 88 and (bottom) Direct Black 88

Conclusion

The results mainly pointed to the characterization of the possible reactive sites of Direct Black 22 and acid red 88, showing that the azo group must play a central role in the chemistry of this dye, acting as a favorable chemical center for electrophilic attacks. The results of this study will be essential to help future investigations where the reactivity of this molecule will be evaluated against the interaction of adsorbents such as Biochar in solution.



Acknowledgment FACEPE, CNPq



Possible mechanism for the uptake of nitric oxide by the Ru(III) antitumor complex NAMI-A

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Palavras-Chave: NO uptake, NAMI-A, CASSCF

The iconic trans [RuCl₄(Im)(DMSO)], known as New Anti-tumor Metastasis Inhibitor-A (NAMI-A), have stood out in bioinorganic chemistry due to its anti-metastatic activity and low cytotoxicity. On average, this compound is more than 100 times less cytotoxic compared to cisplatin, a well-known reference anti-cancer metallodrug. NAMI-A was the first compound to be tested in humans and became a landmark in the field of anticancer metal compounds. However, despite numerous investigations, NAMI-A molecular target and why NAMI-A is inactive in primary tumors are still unknown. It has been suggested that NAMI-A activity against already developed metastases to its anti-angiogenic properties through uptake of Angiogenesis is responsible for the growth of primary tumors from their metastasis and, therefore, identified as a target for pharmacological control of malignant tumors. nitric oxide (NO). NO is expected to participate in the angiogenesis process due to its well-known vasodilation effects, which is of primary importance in the regulation of blood pressure.

In this sense, we use quantum chemical calculations at the Density Functional Theory (DFT) and Complete Active Space Self Consistent Field (CASSCF) level to investigate the mechanism for the uptake reaction of NO by the NAMI-A complex in its mono-hydrolyzed form (NAMI-H₂O). The interaction of the NAMI-H₂O complex with NO was investigated at the theoretical level of B3LYP/def2-TZVP through three possible mechanisms. Two of them were treated in a single Born–Oppenheimer potential energy surface (PES), being exclusively in the singlet or triplet PES. The third possibility involved crossing of both surfaces at one or more reaction points.

By first analyzing the exclusive PES pathways, the results showed that in gas phase only the most stable singlet product is formed with $\Delta G = -30.05 \text{ kcal mol}^{-1}$, while the triplet product formation presents a positive ΔG in the value of $3.16 \text{ kcal mol}^{-1}$. Furthermore, it was possible to observe that the kinetics of singlet PES is approximately three times faster compared to triplet PES. The insertion of the solvent medium at the B3LYP/def2-TZVP/CPCM(SMD) level of theory alters the reaction profile, making the formation of the product spontaneous in both spin states. However, it causes a decrease in the reaction kinetics. As both the NO ($S = 1/2$) and the complex

[RuCl₃(H₂O)(Im)(DMSO)] ($S = 1/2$) have, separately, an unpaired electron, the reactants do not initially exist in a single singlet or triplet state, but in a mixture of both. The multiconfiguration result showed that the most stable electronic structure for the reagent is better described by the DFT/triplet geometry with a wavefunction composed of the average of the singlet and triplet states. This result showed the need to use multiconfigurational calculations such as CASSCF. The same was observed for the transition state, indicating that the reaction mechanism happens first with the rearrangement of atoms and formation of a transition state, and then there is spin coupling. For products, as expected, the total CAS wave function is best described by the 100% singlet state in the singlet geometry. With this information, it is possible to conclude that the corrected mechanism involves a triplet reactant and transition state, with formation of a singlet product. The corrected electronic energies of activation and global show values of 7.53 and -30 kcal mol⁻¹ respectively. To study the transitions between the spin states, it was first determined 3 MECP's (MECP - Minimum Energy Crossing Point), the structural analysis allowed us to conclude that MECP I and II are very similar and, therefore, converge to the same point, totaling two relevant MECP's. Using the CASSCF wave function treatment, it was possible to conclude that the crossing between systems with consequent coupling of the electronic spins must occur at the point of MECP-III, where there will be concomitant NO Ru charge transfer and the formation of the configuration product [Ru^{II}NO⁺]. Our results support the conclusion that NO uptake by NAMI-H₂O may be a possible mechanistic route that justifies the robust antimetastatic activity of NAMI-A, since the concentration of free NO is closely linked with tumor progression through the formation of new blood vessels (angiogenesis). Since NAMI-A is able to uptake NO, its concentration is reduced and, as a consequence, the progression of the malignant tumor is affected. The Gibbs free energy data of activation reveal a relatively low barrier, indicating that the H₂O/NO ligand exchange kinetics is compatible with the reaction rates occurring in biological media.

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Theoretical investigation of the electronic and structural nature of thirteen-atom binary metal cluster of $\text{Ag}_n\text{Bi}_{13-n}$

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Keywords: DFT, nanoclusters, alloys

Introduction

Since Longo and coworkers demonstrated a new synthetic path for Ag–Bi nanoalloys by femtosecond laser irradiation of inorganic oxides $\text{Ag}_2\text{WO}_4/\text{NaBiO}_3$, as well as highlighted its usage as an antimicrobial agent¹, a study of the electronic and structural nature of AgBi nanoclusters from the theoretical perspective is proposed to provide some insights into the physicochemical properties of such materials.

Methodology

All DFT computations were carried using CP2K software (v. 8.1.0)², under PBE level of theory³, employing the Gaussian and plane waves approach (GPW)⁴ along with DFTD3 correction⁵. For the SCF energy, a threshold value of 10^{-7} Ry was chosen, as for the relaxation step the BFGS algorithm was chosen with a maximum force lower than 10^{-3} Ry / atom. For the plane wave section, a grid of 4, cutoff of 650 Ry and grid sampling cutoff of 70 Ry were chosen based upon a convergence of 10^{-7} Ry of those values. Only structures without negative frequencies were considered as local minima and taken for density of states (DOS) and energies calculation.

Results

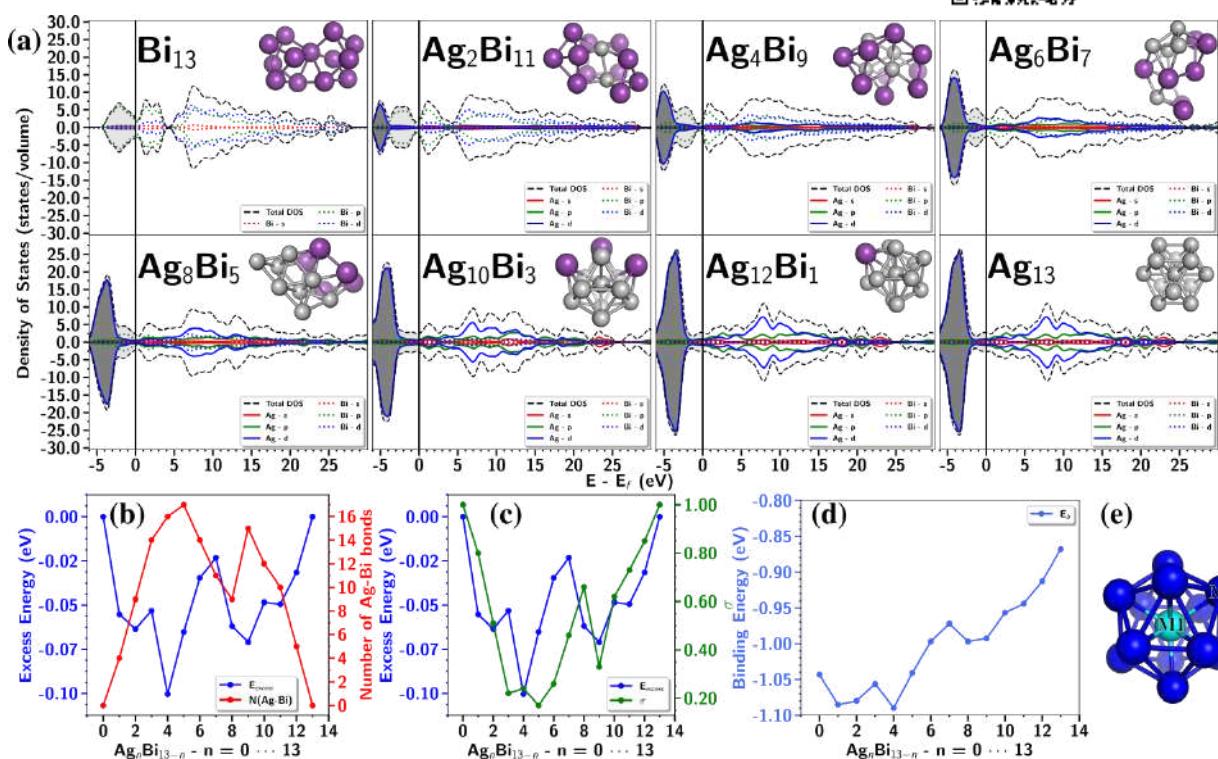
By analyzing the diffusion energy of the system, illustrated by figure (e) we found that for a system of $\text{Ag}_{12}\text{Bi}_1$ where Bi is placed at the **M1** site, migration to **M2** site undergoes with an energy lowering of -0.2306 eV, as for a system of $\text{Ag}_1\text{Bi}_{12}$ the same diffusion process takes 0.2366 eV, this is, Ag prefers to bury itself within the nanocluster structure as Bi tends to migrate to the nanocluster's surface. Thanks to that, the most stable structures found are those in which Bi is found composing mostly of the nanocluster's surface. Nonetheless, as shown by figures (a), (b), (c) and (d) the most stable structure Ag_4Bi_9 presented not only the lowest E_{exc} and E_b but also the best s-d coupling states.

Conclusions

Thanks to the nature of the coupling scheme for bond formation, there is an increase of instability as Ag is added to a Bi pure nanocluster, which is also translated into a higher structural deformation of the system causing the known immiscibility of Bi in Ag systems.

References

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Systematic Study of the Diradical Character of Mesomeric Betaine Derivatives of Heteropentalenes

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Keywords: heterocyclic mesomeric betaines, complete active space self-consistent field, diradical character.

INTRODUCTION

The mesomeric betaines are neutral conjugated molecules which only representations are charge separated resonance structures. The best known heterocyclic mesomeric betaines are the mesoionic compounds. The heteropentalenes are a group of molecules considered as heteroderivatives of the pentalenyl dianion ($C_8H_6^{2-}$). There are ten classes of heteropentalenes. Six of them possess covalent representations and four are heterocyclic mesomeric betaines (Fig. 1).

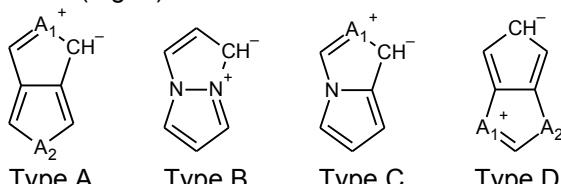


Figure 1. The four types of mesomeric betaine derivatives of heteropentalenes. The groups A_1 and A_2 represent NH, O or S, and we can also replace the carbon atoms by nitrogen.

With the objective of better understanding the electronic structure of betainic heteropentalenes, we are systematically studying the diradical character (y) of such compounds. So far, we considered only molecules with two or less carbon atoms of the rings replaced by nitrogen. This resulted in thirty-six type A compounds, nine type B compounds, forty-eight type C compounds and fifty-seven type D compounds, for a total of 150 calculated molecules.

METHODOLOGY

In our calculations we employed the ORCA5 program. The basis set for all our calculations was the def2-TZVPP and the RIJCOSX approximation was employed in all stages. We first optimized the geometries of all molecules using the spin-component scaled MP2 methodology with the resolution of identity approximation (RI-SCS-MP2). We obtained the diradical character of the molecules from $y=200|c_D|^2\%$ where c_D is the coefficient of the doubly excited determinant of a CASSCF calculation including two electrons and two orbitals. As starting orbitals for the CASSCF calculations, we employed the relaxed density RI-SCS-MP2 natural orbitals obtained during the geometry optimizations. One measure of y , employed in the case of UHF calculations is the singlet-triplet gap (ΔE_{ST}). To compare, we also calculated ΔE_{ST} using the energies of state specific CASSCF calculations corrected by the strongly contracted N-electron valence state perturbation theory (SC-NEVPT2) method.

RESULTS

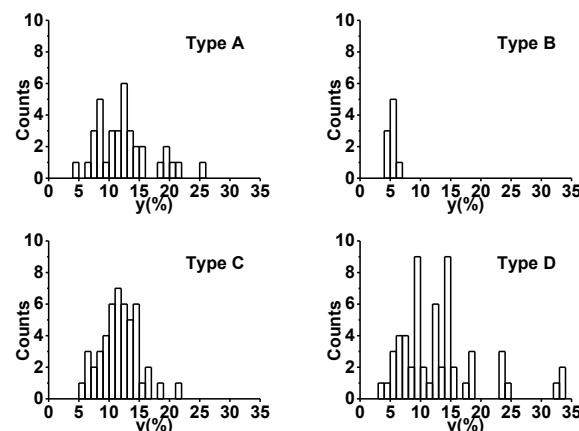


Figure 2. Histograms of the diradical character (y) of the 150 mesomeric betaine derivatives of heteropentalenes studied in this work.

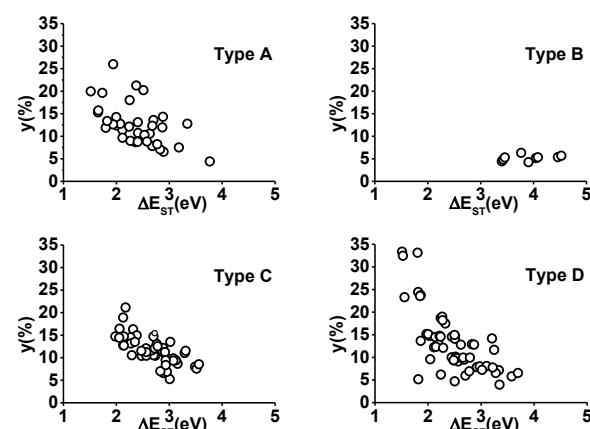


Figure 3. Comparison between the singlet-triplet gap (ΔE_{ST}) and the diradical character (y) obtained using the CASSCF approach.

CONCLUSIONS

We can observe in figure 2 that, in general, the studied compounds have large diradical characters. The type D compounds show the largest standard deviation $\sigma=6.8\%$, followed by the type A compounds with $\sigma=4.6\%$ and the type C compounds with $\sigma=3.2\%$. Three type D compounds with $A_1=A_2=O$ showed the largest values of y around thirty-three percent. All type B compounds studied showed small values of y around five percent with $\sigma=0.6\%$.

We can observe in figure 3 that, apart from the type B compounds (that have little structural variety) there is a weak negative correlation between the diradical character and the singlet-triplet gap.

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Previsão ultra-rápida da estrutura secundária de proteínas a partir de sequências únicas empregando redes neurais profundas

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Palavras-Chave: Bioinformática Estrutural, Inteligência Artificial, Processamento de Linguagem Natural

Introdução

A inteligência artificial inaugurou uma nova era na modelagem biomolecular, trazendo avanços grandiosos na previsão de estrutura de proteínas como observado [1] nas últimas duas edições do experimento CASP. A despeito de alguns darem o problema como “solucionado”, ainda há importantes pontos de avanço no estado-da-arte. Um deles, por exemplo, reside no fato de que, no momento, é necessário fornecer a esses protocolos um alinhamento múltiplo de sequências (MSA) para a proteína-alvo, o que implica na obrigatoriedade de realizar uma custosa busca em bases de dados de sequências e amarra a qualidade do resultado da previsão à profundidade e à diversidade desse MSA. Neste trabalho, propomos a eliminação dessa etapa limitante, objetivando a previsão de uma propriedade estrutural diretamente a partir da sequência-alvo sem necessidade da identificação de homologia remota.

Metodologia

Desenvolvemos e implementamos um modelo de linguagem original que combina elementos de algoritmos clássicos para análise de sentimentos, reconhecimento de imagens e classificação de palavras [2, 3], tratando a sequência de proteínas como uma frase a ser “traduzida” de um idioma de origem (aminoácidos) para um idioma de destino (estruturas secundárias em 3 classes - C, E, H).

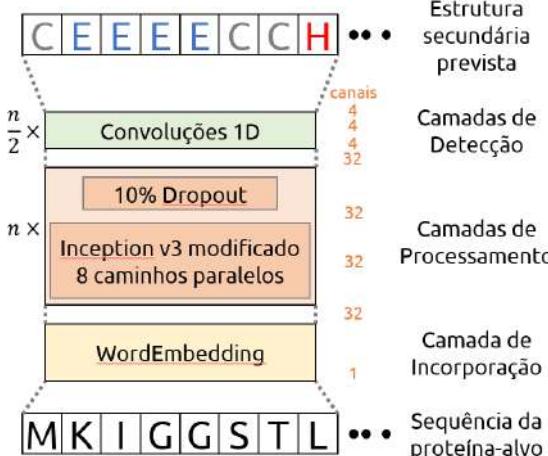


Figura 1. Ilustração da arquitetura empregada

Resultados

O modelo de linguagem implementado neste trabalho melhorou consistentemente os indicadores de desempenho (Q3 / SOV) da previsão de estrutura secundária de um conjunto de aproximadamente 12.000 proteínas não-homólogas em relação aos métodos clássicos de sequência única independentes de homologias. Em alguns casos, a previsão de estrutura secundária para proteínas inéditas para o modelo foi 100% precisa.

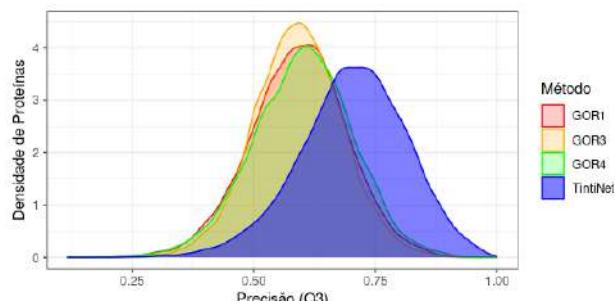


Figura 2. Distribuição da precisão na previsão de estrutura secundária para as proteínas estudadas nos métodos tradicionais (GOR 1, 3 e 4 [4]) e com nosso método (TintiNet)

Conclusões

O uso do modelo de linguagem implementado neste trabalho supera em mais de 10 pontos percentuais a precisão média do método tradicional de sequência única independente de MSA (GOR). Por ser leve, rápido, de código 100% aberto e completamente original, o modelo pode ser implementado mesmo em situações de recursos computacionais limitados.

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Entanglement measures for probing quantum phase transitions in superlattices

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Palavras-Chave: Entanglement, Quantum phase transitions, Superlattices

Model and Methods

One-Dimensional Hubbard Model

$$\hat{H} = \sum_{ij\sigma} t_{ij} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + H.c.) + \sum_i U_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \sum_i v_{i\sigma} \hat{n}_{i\sigma}$$

DMRG - Density Matrix Renormalization Group

Linear Entropy

von Neumann Entropy

$$L(\rho) = 1 - Tr[\rho^2]$$

$$S(\rho) = -Tr(\rho \log_2 \rho)$$

where ρ is the reduced density matrix of single-site.

Superlattices

Superlattices (LS) where LS=36 sites p:q are the periodic impurities = 2:7, 3:6, 4:5 whose impurity1 = 1 to 10 and Impurity 2 = 0 as noted Fig.1. In Fig.2 we compare DFT to DMRG for several p:q.

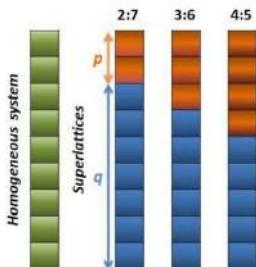


Figure 1: Schematic representation of the homogeneous system and of the investigated superlattices, where p:q vary.

Conclusion

- We find that DFT is reliable tool for superlattices (Fig.1).
- Our results show that the two entropies vary considerably, even qualitatively, for small modulations ΔV (Fig.2)
- In the interval where the quantum phase transitions occur, the entropies have different behaviors (Fig.2 and Fig.3).

Acknowledgment



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Araraquara



Results

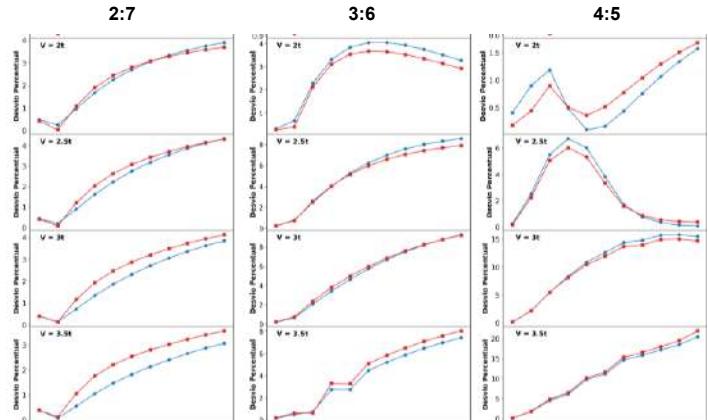


Figure 2: Percent deviation for 36-site superlattices with p:q=2:7, 3:6 and 4:5 as a function of the U interaction.

2:7

3:6

4:5

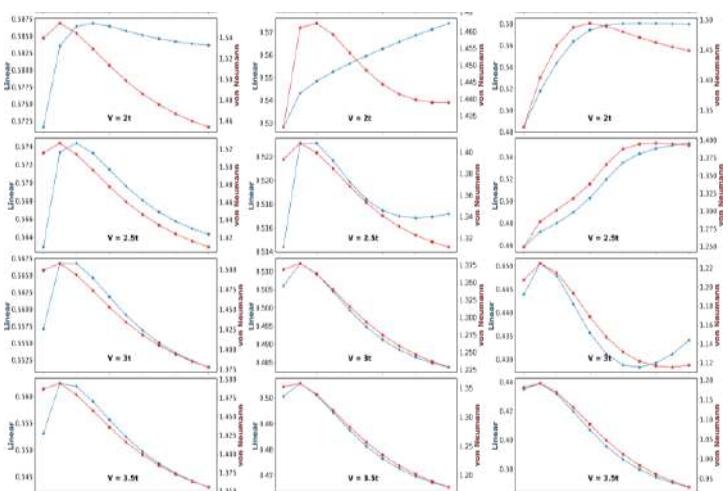


Figure 3: Quantum phases transitions for DMRG.

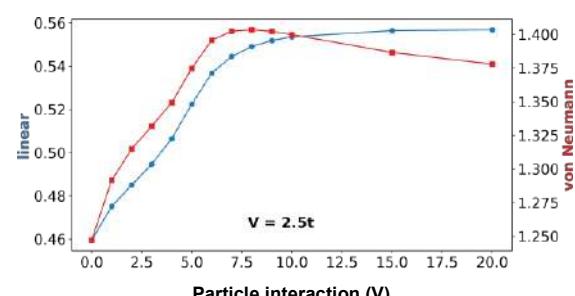


Figure 4: Comparison between the mean entropies as a function of the Coulomb interaction (U) for a 4:5 superlattice with 36 sites, under a V=2.5t.

DFT studies and Hirshfeld analysis of a new Tutton salt crystal

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Keywords: Tutton salt, DFT, Hirshfeld surface analysis.

INTRODUCTION

Tutton salts are a class of crystals with isomorphic structures and a typical composition $[M^{2+}(A^+)_2(H_2O)_6(SO_4)_2]$, where M is a transition metal and A is a counter cation. Recent theoretical studies show that this structure is due to the instability caused by the electric field of the internal lattice.¹ In this work, we performed a theoretical study of the Tutton salt $(NH_4)_2[Mn(H_2O)_6](SO_4)_2$ to elucidate its structural and electronic properties.

METHODS

The full geometry optimization and vibrational frequencies calculations were performed for the coordination complex using the functional B3LYP, as implemented in *Gaussian16* software.² The basis set 6-31G(d) was used for H and O atoms, and the pseudo-potential Stuttgart-Dresden (SDD) was used for Mn²⁺, with charge +2 and spin multiplicity 4. Furthermore, the Hirshfeld surface analysis was obtained with *CristalExplorer*.³ The results were analyzed using the graphical interface program *Chemcraft1.8*.

RESULTS

From the optimized geometry of the complex (Fig. 1a), we obtained partial atomic charges, electrostatic potential map and the frontier molecular orbitals HOMO and LUMO. The representative intermolecular interaction of crystal lattice was obtained from a cluster centered in metal complex and surrounded by their counterions. The metal complex structure has a slightly distorted octahedral geometry. The HOMO-LUMO energy gap of the complex is 3.68 eV. The Hirshfeld surface analysis (Fig. 1b) reveals that the sulfate anions interact

directly with the metal complex through hydrogen bonds that represent 53% of all interactions established, followed by 37% due to ammonium cation H···H contacts, and 9.8% due to hydrogen bonds between the O atoms of water, and the H atoms of ammonium cation.

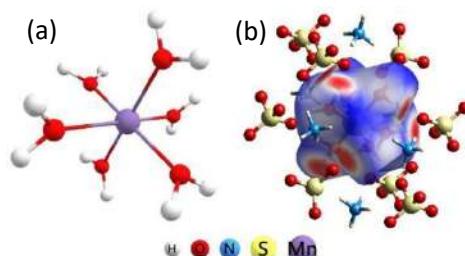


Figure 1. Optimized geometry (a) and Hirshfeld surface of $(NH_4)_2[Mn(H_2O)_6](SO_4)_2$ (b)

CONCLUSION

The Tutton salt investigated here presented relative instability due to the low HOMO-LUMO energy gap. The analysis of the electronic properties provides the preferred sites for intermolecular interactions. Hirshfeld surface analysis reveals the importance of intermolecular interactions in the stabilization of the compound.

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ACKNOWLEDGMENTS

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Interações entre folhas de grafeno pura e dopada e gases do efeito estufa sob a luz de métodos de análise de ligações

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Palavras-Chave: Grafeno, Dopagem, Gases do efeito estufa.

Introdução

Dentre os diferentes sensores de gases fundamentados em semicondutores, o grafeno apresenta grande destaque neste assunto, devido a sua precisão na detecção de uma variedade de gases. Neste contexto, a dopagem do grafeno com outros elementos pode alterar as suas propriedades superficiais. Dessa maneira, o grafeno dopado corretamente pode ser utilizado como sensor para gases do efeito estufa à base de nitrogênio (NH_3 , NO e NO_2). De acordo com a literatura [1], a dopagem do grafeno com elementos do grupo 13 da tabela periódica (Boro e Alumínio) pode melhorar a interação da folha de grafeno com esses tipos de gases, tornando-a um bom material sensível aos gases do efeito estufa a base de nitrogênio. A partir disso, o estudo teórico computacional, do ponto de vista de ligação química, pode ajudar na compreensão do comportamento dos pares ácido-base, formados entre superfícies de grafeno puro e dopada com os gases a base de nitrogênio.

O objetivo deste trabalho é reportar o estudo computacional das interações ácido-base de Lewis entre folhas de grafeno puras e dopadas e os gases do efeito estufa a base de Nitrogênio (NH_3 , NO e NO_2), comparando os resultados obtidos através do modelo de recobrimento (OP) [2], da Teoria Quântica de Átomos em Moléculas (QTAIM) e da Teoria dos Modos Locais de Vibração (LVM) [3].

Metodologia

Todos os cálculos de geometria, ponto único e frequência foram feitos em $\omega\text{B97X-D/6-311++G(d,p)}$, usando o programa Gaussian09. Os orbitais moleculares localizados, necessários para as análises de recobrimento, foram obtidos usando o método Pipek-Mezey (GAMESS). As propriedades de recobrimento (cargas ρ_{op} e repulsão J_{OP}^{intra}) foram calculadas usando nosso software ChemBOS. As análises QTAIM foram feitas no software Multiwfn. E por fim, as constantes de força dos modos locais de vibrações foram obtidas usando o software LmodeA.

Resultados e discussão

A Tabela 1 mostra os resultados obtidos com os três métodos de análise de ligações químicas. Observa-se a interação do NO com o Grafeno (G) se dá com interação mais forte (k_n^a maior) para o Al@G. Associado a isso, tem-se valores maiores do J_{OP}^{intra} e ρ_{op} , indicando maior concentração de carga nessa interação, em comparação com a NO...B@G. Por outro lado, a densidade no ponto crítico da densidade

eletrônica total não se altera para as interações NO...Al@G e NO...B@G, sendo o laplaciano no ponto crítico da primeira maior, o que indica depleção de carga na ligação, em comparação com a segunda. Adicionalmente, observa-se que o QTAIM fornece resultados similares para a interação do NO sem dopante (NO...@G) e com (NO...Al@G e NO...B@G), o que não se observa nas análises OP e LVM.

A folha de grafeno dopada com boro, segundo a análise LVM, interage mais fortemente na ordem $\text{NO} < \text{NH}_3 < \text{NO}_2$.

Tabela 1. Propriedades das interações químicas estudadas. Constante de força de modo local k_n^a (mDina/Å) repulsão de intrarecobrimento J_{OP}^{intra} (E_h), densidade de recobrimento ρ_{op} (e), densidades eletrônicas ρ_{BCP} (e/a^3), laplaciano $\nabla^2\rho_{BCP}$ (e/a^5)

Sistemas	k_n^a	J_{OP}^{intra}	ρ_{op}	ρ_{BCP}	$\nabla^2\rho_{BCP}$
NO...Al@G	0,77	3,52	0,43	0,06	0,21
NO...B@G	0,41	0,99	0,23	0,06	0,09
$\text{NH}_3\cdots\text{B}@G$	0,94	9,35	0,74	0,09	0,23
$\text{NO}_2\cdots\text{B}@G$	1,17	8,82	0,71	0,11	0,12
NO...@G	0,10	0,01	-0,02	0,01	0,02
NO...@G	0,06	0,05	0,06	0,01	0,02

A Figura 1 apresenta as densidades de recobrimento para as interações do NO com o grafeno dopado e puro, em que se observa a interação com concentração de densidade eletrônica.

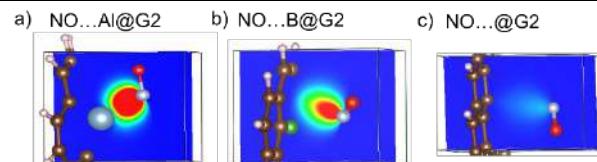


Figura 1. Mapas de densidade dos sistemas grafeno-gás com o gás NO, em mapa de cores RGB na faixa $0 – 0.01665 e/a_0^3$.

Conclusões

A folha de grafeno dopada com boro, segundo a análise LVM, interage mais fortemente na ordem $\text{NO} < \text{NH}_3 < \text{NO}_2$.

Agradecimentos

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Proposition of Cr^{3+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} complex structures with glycine: A structural and electronic approach

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Keywords: Glycine complexes, DFT, Complex structures of aminoacids.

Introduction

Amino acids are the building blocks of our cellular machinery in the form of proteins and protein complexes, they play various functional, structural, metabolic, and developmental roles in the body. The amino acids, for convention, have been divided into two categories: indispensable (or essential) and dispensable (or non-essential) (Schaafsma, 2000). Glycine is the smallest non-essential, neutral and metabolically inert amino acid, with a carbon atom bound to two hydrogen atoms, and to an amino and a carboxyl group (Pérez-Torres et al., 2016). Glycine plays an important role in human body, has anti-inflammatory properties, improves immunity, enhance anti-oxidative capacity and in central nervous system it has a crucial role as neurotransmitter (Pérez-Torres et al., 2016; Razak et al., 2017). Some complexes of glycine can therefore occur as studied by Yahia and collaborators (Hamada, et al., 2017) and propose the structures based on both electronic and structural properties is the scope of this project (Figure 1).

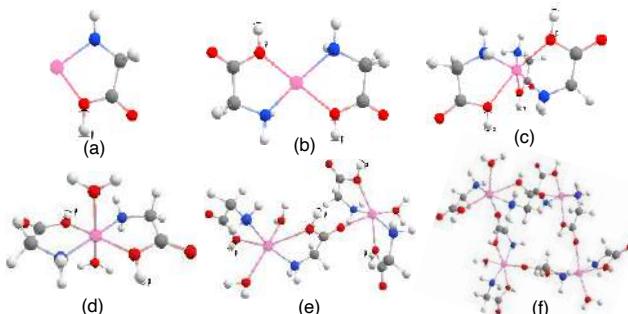


Figure 1 – Complexes representations. Atoms are colored by elements: Blue-Nitrogen, Red-Oxygen, gray-Carbon, White-Hydrogen and pink for metallic centers (Cr^{3+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}).

Methodology

The optimizations were carried out with DFT functional wb97XD and 6-311+G(2d,p) basis set for all atoms including the metallic centers. Frequency calculations and population analysis were also evaluated on optimized structures in order to study electronic properties of the systems. The results were described using AOMix software package. An AIM and NBO study were performed to better understand the dynamics of electron donation and acceptance. All optimizations, frequency calculations and population analysis were performed with Gaussian 09 in the very same level of theory.

Results and discussion

The initial proposed structures are the ones shown on figure 1; some as Zn, Mn, Fe, Cr-Gly₂ (b) acquired a tetrahedron geometry. NBO calculation showed an overall stabilization between metallic center and glycine. Figure 2 illustrates NBO superposition in square planar Cu-Gly₂. Furthermore, N NBOs were showed stabilizing the system twice as strong as O NBOs.

Molecular orbitals were also evaluated and figure 3 shows HOMO-LUMO for octahedral Zn-Gly₂. Varies from 10.774eV, on figure 1-a, to 11.330eV for the system mentioned on figure 3.

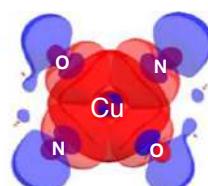


Figure 2-NBO representation for cooper square planar complex (Figure 1-(b)).

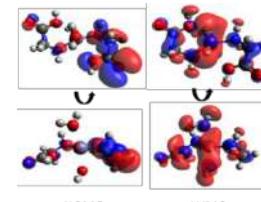


Figure3 - HOMO-LUMO illustrations of octahedral Zn(II) complex with two Gly and two water molecules (Figure 1-(d))

According to an AIM appraisal which focused on both ring and bond strains analysis, Zn-Gly and Cu-Gly are the most stable among the structures on figure 1a and protonated Cr-Gly showed itself as the most structural unstable. Bader's atomic charges were also analyzed and confirms that protonated species have higher charge over metal ion than the deprotonated ones.

Conclusions

The geometries achieved in this project demonstrated stability, which were discussed based on structural and electronic properties. In general, the interaction energy does not get lower with more glycine ligands in any metallic centers. The energy gap between the frontier molecular orbitals fluctuates about 1eV. All results are concise to each other and demonstrates the stability of those complexes.

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Caracterização computacional do mecanismo de acoplamento cruzado C–C via dupla ativação das ligações C–O de éteres catalisado por Ni

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Palavras-Chave: Cálculos DFT, Acoplamento C-C, Catálise por Ni.

Resumo e Introdução

A ativação ou clivagem da ligação C–O é uma excelente estratégia para se promover reações de acoplamento cruzado de eletrófilos oxigenados¹. Shi e Cao² desenvolveram uma metodologia de formação de ligações C–C entre os fragmentos carbônicos de éteres, através de sua desoxigenação catalisada por Ni(dppb), na presença pô de zinco (redutor) e de Bis(pinacolato)diboro (B₂pin₂). A proeminência dessa metodologia está na sua boa economia de átomos, desde que a clivagem das duas ligações C–O possibilite que os dois esqueletos carbônicos do reagente concebam o produto desejado. Assim, nesse estudo caracterizou-se em nível DFT/M06L o mecanismo dessa reação de desoxigenação de éteres. O ciclo catalisado por Ni possui 5 eventos, respectivamente denominados de 1^a adição oxidativa, redução, 2^a adição oxidativa, redução e eliminação redutiva. A 2^a adição oxidativa contém a região determinante da cinética da reação com uma barreira de, ΔG^\ddagger , igual a 32,2 kcal/mol. Ademais, se determinou que o B₂pin₂ atua na ativação da segunda ligação C–O, mediante sua reação com o grupo alcóxido proveniente do éter. Esse grupo é gerado, complexado a um cluster de Zn, nas etapas de redução do ciclo catalisado por Ni. No processo referente à segunda ativação C–O, forma-se um radical alquila composto por um dos fragmentos carbônicos do substrato, esses, por sua vez, reagem com complexos de Ni e formam espécies comuns ao ciclo Ni catalisado.

Metodologia

Os cálculos em nível DFT/M06L, em que os átomos foram descritos pelos conjuntos de bases SDD (Ni), LANL2DZ (Zn) e 6-31G** (C, H, O, P, B). Estruturas de equilíbrio e de transição foram caracterizadas por cálculos de frequência vibracional. A correspondência dos TS entre reagentes e produtos foi confirmada por cálculos de IRC. O pô de zinco foi descrito por um cluster de Zn₁₆. Todos os cálculos foram realizados em fase de gás no programa Gaussian09.

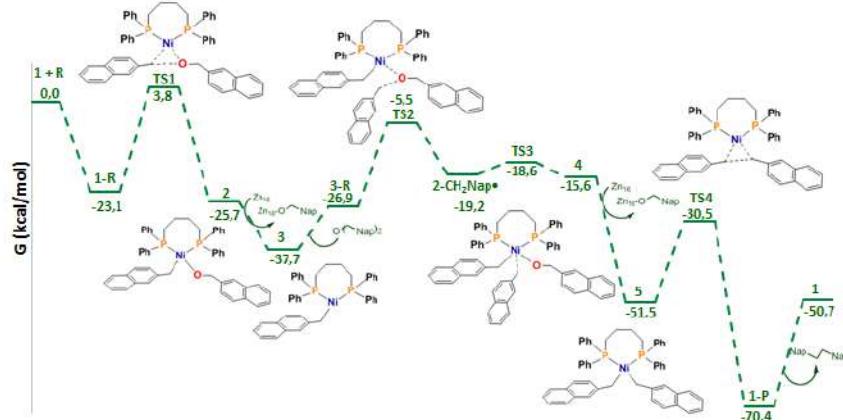


Figura 1. Perfil de energia livre, em kcal/mol, referente ao mecanismo de desoxigenação do éter 2,2'-Naphthyl.

reage com Zn₁₆–OR formando Zn₁₆–O(B₂pin₂) + R•, com uma barreira limitante de 21,0 kcal/mol. Os radicais alquilas são inseridos ao ciclo catalisado por Ni via as reações 2 + R• → 4 e 3 + R• → 5.

Conclusões

A barreira de $\Delta G^\ddagger = 32,2$ kcal/mol para o ciclo catalisado por Ni é concordante com a temperatura da reação de 115 °C e a formação do produto C–C, mesmo na ausência do B₂pin₂. O B₂pin₂ atua na ativação da segunda ligação C–O e gera radicais alquilas que se conectam ao ciclo Ni catalisado.

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Ab initio study on the reactions of phosphorus-bearing molecules in the interstellar medium

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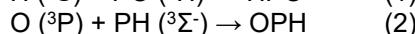
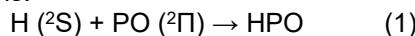
Key words: astrochemistry, molecular formations, ab initio studies

1. INTRODUCTION

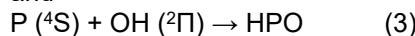
The chemistry of interstellar phosphorus is still currently unknown at its fullest. As phosphorus is the fifth main component in biological systems (coming after hydrogen oxygen, carbon, and nitrogen), it plays an important role to life as we know it, especially when bonded as P-O in DNA, RNA and ATP (Turner et al. 2018; Rivilla et al. 2016). Therefore, the knowledge of its origins and chemical evolution is relevant not only to astrochemistry, but also to the astrobiology field.

Since PO has been found in the interstellar medium and in the circumstellar envelope of oxygen-rich (O-rich) stars (Turner et al. 2018; Rivilla et al. 2016; Lefloch et al. 2016; Tenenbaum et al. 2007), the reactions concerning the radical have been posing a great lead on the development of our knowledge of this element of great importance for life.

In the present work we investigate the reactions:



and



which may provide an idea of the source of PO found in gas phase in O-rich envelopes (Turner et al. 2018; Rivilla et al. 2016).

1. AB INITIO METHODS

The calculations were performed using the MOLPRO package. Singlet and triplet energies were reported here, employing the state-averaged complete active space self-consistent field (CASSCF). The calculations were done for the two least energetic states of each symmetry under the C_s point group.

The full valence active space consisting of 12 electrons in 9 orbitals was employed with the aug-cc-pV(T+d)Z basis set. Potential energy scans were first done at fixed angles of 0, 30, 60, 90, 120, 150 and 180 degrees in the search for potential minima and transition states. Geometry optimizations were carried out to locate the stationary structures.

2. RESULTS

After preliminary analysis of the reactions with fixed attacking angles, the minima and

transition states had their geometries optimised and their frequencies calculated.

The calculations show that the reactions occur without potential barriers, except for the triplet state of reaction (1). A conical Intersection was also located. Our major conclusions are that reaction (2) can fastly deplete the PH molecule in O-rich environments, and that PO is stable with respect to collisions with atomic hydrogen, the most abundant species in the ISM. It was noted that all three reactions end with the same product, the HPO specie. Reaction (2) is exothermic by 224,85 kJ/mol and the reaction (3) is exothermic by 112,11 kJ/mol. Those energies were compared to the stable H+PO product achieved throughout the calculations.

3. CONCLUSION

The calculations show promising results for the CASSCF method, and further calculations with the MRCI method and the aug-cc-PV(5+d) Z basis set are currently being made to provide more precise energy values.

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Oxidação da ciclopentanona: um estudo mecanístico

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Keywords: Cinética química, Teoria do Estado de Transição, DFT, Combustão.

O uso de alguns aditivos ao combustível de motores à combustão interna foi proposto para contornar alguns problemas, como por exemplo a queima não-homogênea do combustível dentro do cilindro. O grupo das ciclocetonas mostrou-se ser uma alternativa promissora como aditivo, e dentre estas temos a ciclopentanona. Neste contexto, este trabalho tem como principal objetivo a determinação dos parâmetros energéticos e cinéticos para as reações envolvidas no processo de combustão da ciclopentanona [1-2].

(**Pa** e **Pb**) através de 4 estados de transição diferentes. Em seguida, foram propostas reações de abertura de anel para estes radicais, originando 4 novos intermediários. Nesta etapa, uma busca conformacional no nível deste estudo identificou 7 confôrmeros distinguíveis para o intermediário **A15**, 4 confôrmeros para **A34**, 10 confôrmeros para **B12** e 3 confôrmeros para **B54**. A partir destes intermediários, três canais de dissociação foram propostos.

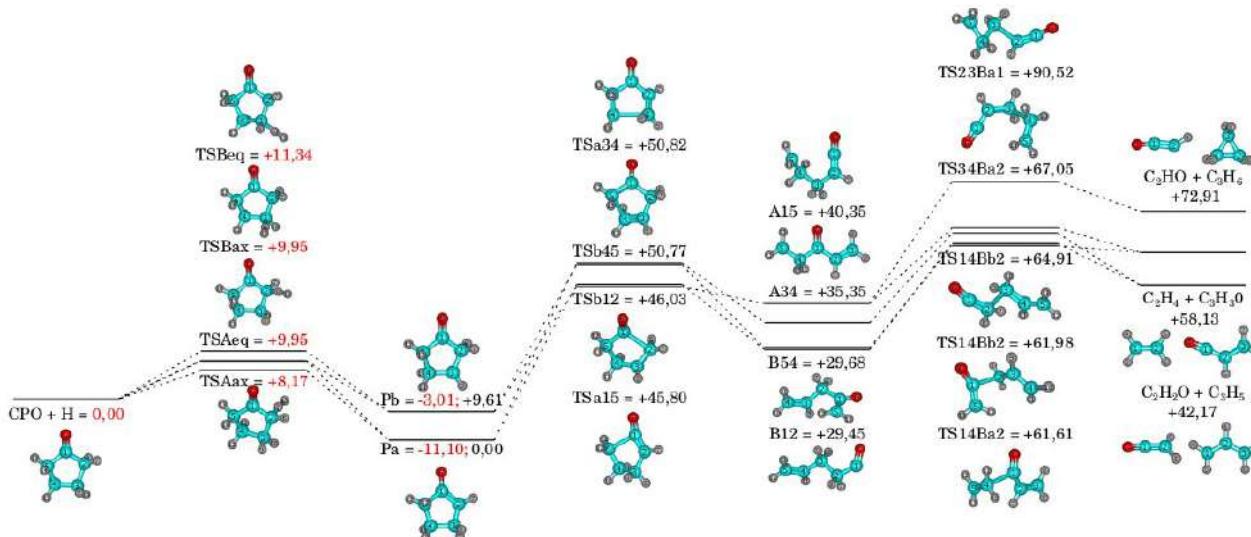


Figura 1. Perfil energético para a combustão da ciclopentanona (CPO), determinadas no nível de teoria M06-2X/6-31+G(d,p). Em vermelho as energias relativas aos reagentes reação de abstração de hidrogênio (CPO + H), e em preto as energias relativas ao radical **Pa** para as reações unimoleculares. Diferenças de energia em kcal/mol.

Numa primeira etapa, foi construído um *benchmark* energético para a validação do método de estrutura eletrônica a ser utilizado. Nessa avaliação, diferentes pares de funcionais e conjuntos de bases atômicas foram avaliados frente a aproximação altamente correlacionada CCSD(T)/CBS (aug-cc-pVQZ e aug-cc-pVTZ). O nível de teoria com menor erro absoluto médio encontrado foi M06-2X/6-31+G(d,p). Todos os cálculos de estrutura eletrônica foram realizados utilizando o GAUSSIAN09 e o MOLPRO 2010. A Figura 1 ilustra o perfil energético encontrado para o mecanismo de combustão da ciclopentanona, no qual estão representados os confôrmeros mais estáveis para mínimos e estados de transição. Como primeira etapa do mecanismo, as reações de abstração de hidrogênio da ciclopentanona pelo radical H que gera os radicais

Como uma próxima etapa, este estudo fará a obtenção das constantes de velocidade de todas as etapas elementares deste mecanismo e, avaliará a influência da inclusão de múltiplas estruturas e da anarmonicidade torsional na distribuição dos produtos deste mecanismo de combustão.

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Molecular modeling of new 1,2,4-oxadiazoles-3,5-dissubstituted compounds.

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Palavras-Chave: molecular docking, oxadiazoles, antimicrobial activity.

Introduction: 1,2,4-oxadiazoles compounds were recently emerged as a promising class of drugs with antibacterial, antimalarial, and antifungal activity [1]. Recent development of new synthetic routes to obtain 1,2,4-oxadiazoles-3,5-dissubstituted shows high yield (40-97%) and good bacterial activity against Gram-positive (*S. aureus* and *E. faecalis*) and Gram-negative (*P. aeruginosa* and *K. pneumoniae*) bacteria [2]. These compounds can be powerful agents to fight against antibiotic resistance [3] In order to access structural and electronic effects involved on inhibitory process of these compounds theoretical studies were carried out in order to investigate qualitative aspects.

Methodology: We carried out molecular docking and DFT calculations on 1,2,4-oxadiazoles structure derived from the scheme below:

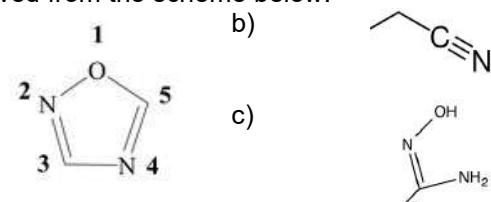


Figure 1: (a) Structure of a 1,2,4-oxadiazole ring; Position 5 could be occupied by a methyl-nitrile (b) or amidoxime group (c); Position 3 could be occupied by nine different substituted aromatic rings involving a total of 18 investigated compounds.

Molecular docking calculations were performed for 18 oxadiazoles using Autogrid [4] and Autodock [5] softwares against X-ray structures of *Penicillin Binding Proteins* (PBPs) retrieved from Protein Data Bank (PDB IDs: 4CJN, 6IJE, 2OV5, 6MKI). Ligand structures were built in PubChem website. We used a gridbox of 126 Å x 126 Å x 126 Å and spacing of 22 Å. We adopted a Lamarckian algorithm with an initial population of 150 individuals/generation and maximum number of 27,000 generations, and a total of 2.5×10^7 energy evaluation/generation. Mutation and crossover rates corresponded to 0.02 and 0.08, respectively. We choose 50 docking runs for each calculation. We also performed DFT (Density Functional Theory) optimization, frequency, and orbital frontiers calculations for the ligands at WB97XD/6-311G(d,p) theory level. **Results** When

we compare our docking results against available antimicrobial measurements [2], it is possible to confirm the disubstituted oxadiazole with methyl-nitrile and p-chlorobenzene as the most promising synthesize compound.

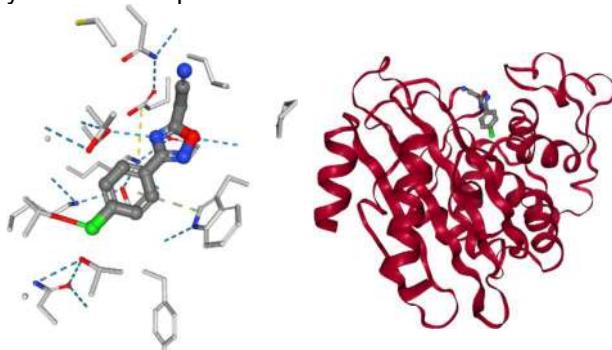


Figure 2: Close on docked structured on 2OV5 active site (left) and protein plus ligand structure (right).

We noted a prominent number of hydrogens bonds, hydrophobic and attractive contacts between this ligand (Figure 2) and active sites in comparison to the others oxadiazoles compounds. A moderate relationship can be established between the HOMO-LUMO values of the compounds and their antimicrobial effects against PBPs. One of the least active compounds has the highest quantum parameters with $\Delta E = 0.17513$ a.u. **Conclusions:** We have set a molecular docking protocol able to reproduce qualitatively experimental inhibition measurements and provide some structural and electronic explanations between ligands and active site. We have started to set up atomistic molecular dynamics simulations in order to investigate dynamics aspects of the interaction of the most promising compounds and PBPs of Gram-negative and Gram-positive bacteria. **References:**

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Estudo Teórico de Diferentes Canabinóides Encontrados na *Cannabis Sativa*

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Palavras-Chave: *Cannabis sativa*, sistema endocanabinóide, maconha, DFT, HPCCS.

Introdução

A *Cannabis sativa* tem sido cultivada pelo homem há mais de 5.000 anos, tanto para a obtenção de fibras, quanto para fins medicinais ou recreativos. A maconha, nome popular da planta, apesar de sua longa história na humanidade, é marginalizada e pouco explorada no Brasil. Recentemente, os canabinóides tem sido explorados devido seu enorme potencial medicinal e recreativo, com baixos níveis de toxicidade e/ou efeitos colaterais, em vários países de todos os continentes.¹

O sistema endocanabinóide humano, possui diversos receptores canabinóides, especialmente receptores de membrana ligados a proteína G. A ativação desses receptores, tipicamente, inibe a adenilato-ciclase com consequente fechamento dos canais de cálcio, abertura dos canais de potássio e estimulação de proteínas quinases. Cada canabinóide presente na *Cannabis* interage de maneira distinta com o sistema endocanabinóide, provocando diferentes efeitos no organismo.²

A maconha é composta de diversos tipos de canabinóides, sendo os mais comuns o Tetrahidrocannabinol (THC) e o Canabidiol (CBD). O THC se destaca pelos efeitos psicoativos, sendo a principal molécula explorada para uso recreativo da planta. Já o CBD apresenta diversas aplicações terapêuticas, tendo sido amplamente utilizado em tratamentos de doenças psiquiátricas ou neurodegenerativas, esquizofrenia, mal de Parkinson, epilepsia, dentre outros.²

O mercado legal da *Cannabis* movimentou em 2020 cerca de 21,3 bilhões de dólares no mundo. Junto com esse mercado, houve um crescimento expressivo na necessidade de análise desses compostos, dos pontos de vista qualitativo e quantitativo. Separar e analisar os produtos recreativos e medicinais é algo de extrema importância, sendo necessário utilizar técnicas cromatográficas de ponta.³

Objetivos

Tendo em vista todo esse panorama da maconha no mundo e a potencial expansão do mercado, este trabalho tem por objetivo o estudo químico dos principais canabinóides encontrados na *Cannabis sativa*. Cálculos envolvendo a Teoria do Funcional de Densidade (DFT) e simulações clássicas foram realizados para descrever a estrutura

eletrônica e obter informações sobre a seção de choque (CCS) para as moléculas.

Metodologia

Foram estudadas um total de 21 canabinóides, sendo todos encontrados em maior ou menor quantidade em diferentes espécies de maconha. A Teoria do Funcional de Densidade, no nível M06-2X/6-31+G(2d,p), foi utilizada para otimização e análise das frequências vibracionais das estruturas. As cargas de Mulliken, obtidas desses cálculos, foram utilizadas para obtenção das cargas atômicas individuais. Os cálculos foram realizados com o programa Gaussian 09⁴.

Os cálculos da seção de choque foram obtidos com o pacote HPCCS (*High Performance Collision Cross Section*)⁵, que utiliza do método de trajetória para simular as colisões. Tais cálculos podem ser utilizados para interpretar a mobilidade molecular, o que pode ser utilizado na interpretação dos resultados cromatográficos, especialmente da técnica de mobilidade iônica acoplada a espectrometria de massas (IMS-MS).

Resultados

Resultados preliminares, para as moléculas de THC e CBD, são apresentados na Figura 1, que apresenta as estruturas otimizadas com diferentes informações obtidas pelos cálculos realizados.

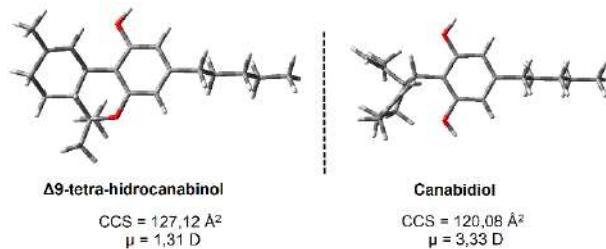


Figura 1: Moléculas de THC (esquerda) e CBD (direita) otimizadas e suas informações moleculares.

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Computational studies on inhibition of vivapains of *Plasmodium vivax*

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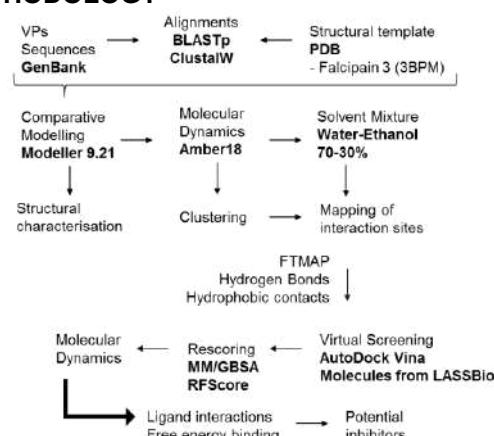
Keywords: *malaria, drug design, molecular dynamics*

INTRODUCTION

Two parasite species cause together 95% of all malaria cases. They are *Plasmodium falciparum* and *P. vivax*. Increasing resistance to treatment against *P. vivax* infection difficults its combat around the world. New biological targets and pharmacological molecules must be explored to overcome that. In *P. vivax*, the proteins responsible for breaking haemoglobin, providing amino acids for the replication of the parasite inside lysosomes are the vivapains (VPs).

Here, we study the anti-malarial targets enzymes VPs, specially the vivapain-4 (VP4), aiming to explore its sites for guiding virtual screening assays to identify potential new inhibitors.

METHODOLOGY



RESULTS

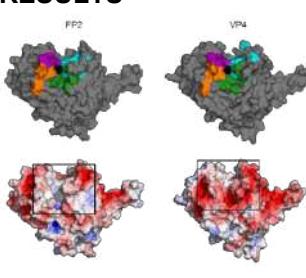


Figure 2: Crossclusters of fragments docked at the catalytic site of VP4. In evidence, residues with the most interactions involving hydrogen bonds or non-bonded contacts.

For comparative modelling, it was identified that falcipains 2 and 3 and the vivapains 2,3 and 4 present identity of at least 54% and with similarity higher than 80%. It was observed that the mutation Ala → Glu at

position 177 of VP4 implies changes in the electrostatic surface of the protein at their catalytic site (Figure 1). The docking of small molecules at FTMAP server with the representative structures from MD of VP4 identified residues Gly38, Tyr159, His176, Trp208 as more important for their interactions (Figure 2). With the mapping with mixed solvent simulations, residues Tyr159 and 208 were extremely relevant, presenting more than 50% of prevalence during the simulations. VS evaluation from MM/GBSA (Figure 3), led us to identify the most interesting ligands, involved with such residues and further analysed by MD simulations, such as LASSBio1804 and LASSBio1723 (Table 1 and Figure 4).

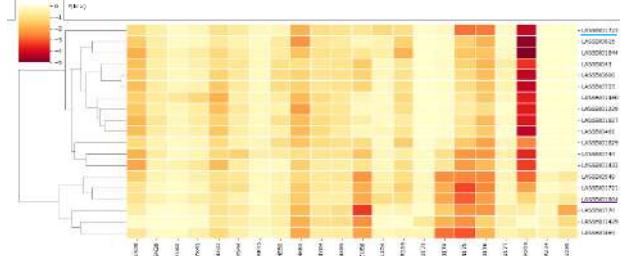


Figure 3: Heat map of free energy binding of Top20 ligands from VS interacting with catalytic residues of VP4.

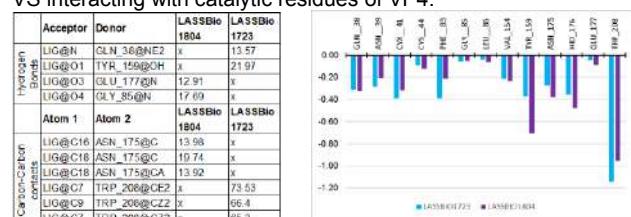
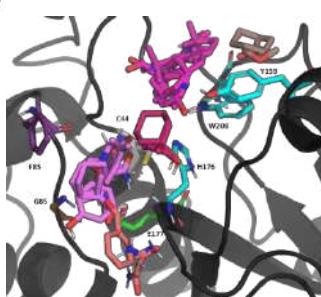


Table 1: Most prevalent hydrogen bonds and hydrophobic contacts from MD with ligands LASSBio1804 and LASSBio1723.

Figure 1: Enzymes FP2 e VP4, catalytic site in evidence. Em cima: catalytic subsites (**S1**, **S1'**, **S2** e **S3**). Embaixo: electrostatic surface.



CONCLUSIONS

The results among the different strategies allowed the identification of residues most involved in ligand interactions, and of potential lead molecules for binding sites of VP4. Optimisation combining both ligands is desired.

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Estudo computacional da interação de Na^+ em nanofolhas de nitreto de carbono grafítico ($\text{g-C}_3\text{N}_4$) solvatadas em água

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Palavras-Chave: Nitreto de carbono grafítico, Poliimida de Heptazina e dinâmica molecular.

Introdução

O nitreto de carbono grafítico ($\text{g-C}_3\text{N}_4$) é um polímero semicondutor repleto de anéis nitrogenados e que possui uma estrutura em camadas, sendo promissor para fotocatálise na região do UV-Vis e fabricação de sensores [1]. Em geral, os anéis nitrogenados podem ser de dois tipos: anéis de triazina (PTI) e anéis de heptazina (PHI), entretanto, de acordo com os nossos experimentais, o $\text{g-C}_3\text{N}_4$ sintetizado em NaCl líquido, possui além dos anéis de heptazina, uma cavidade maior, que confere carga negativa ao material, sendo neutralizada por Na^+ . Contudo, não há informações experimentais sobre em que regiões o Na^+ tende a interagir melhor com cada folha, sendo assim, o presente trabalho tem como foco explicar esta questão por meio de simulações de dinâmica molecular clássica.

Metodologia

Um modelo inicial deste material foi desenhado com 5,5 nm de aresta, contendo 6 cavidades maiores, resultando em uma estrutura com carga total de -18. Caixas de simulação de 8,0 nm de aresta foram construídas, onde cada sistema de PHI com até 3 camadas foi solvatado com cerca de 16 mil moléculas de água. As posições iniciais do Na^+ bem como a distância e inclinação inicial entre cada folha foram determinadas através do software Themis [2], usando como critério a energia livre.

Após isso, foram realizadas dinâmicas moleculares no pacote computacional GROMACS [3], usando o campo de força CHARMM36 [4], onde, inicialmente foi realizada uma minimização de energia, seguida de uma dinâmica NVT de 150 ps a 298,15 K, e por último, foi realizada uma dinâmica NPT de 200 ns, à 298,15 K e 1 bar. A trajetória da dinâmica NPT foi utilizada para se realizar a análise da distribuição radial de pares (RDF) entre o Na^+ e os N de cada poro, desprezando os 150 ps iniciais.

Resultados

As RDFs das Figuras 1(a), 1(b) e 1(c) mostram que há uma maior tendência do Na^+ ficar nos poros menores, na monocamada. Porém, as RDFs das Figuras 1(g), 1(h) e 1(i) mostram que em sistemas com mais camadas o Na^+ tende a migrar para os poros maiores. Os picos em torno de 0.4 das RDFs das Figuras 1(d), (e) e (f) mostram justamente que o Na^+ não tende a ficar no centro da aresta do poro maior, mas sim um pouco mais próximo dos vértices, como mostram as RDFs das Figuras 1(g) e (h). Vale ressaltar também que nesta distância também há Na^+ nos poros menores em ambos os sistemas.

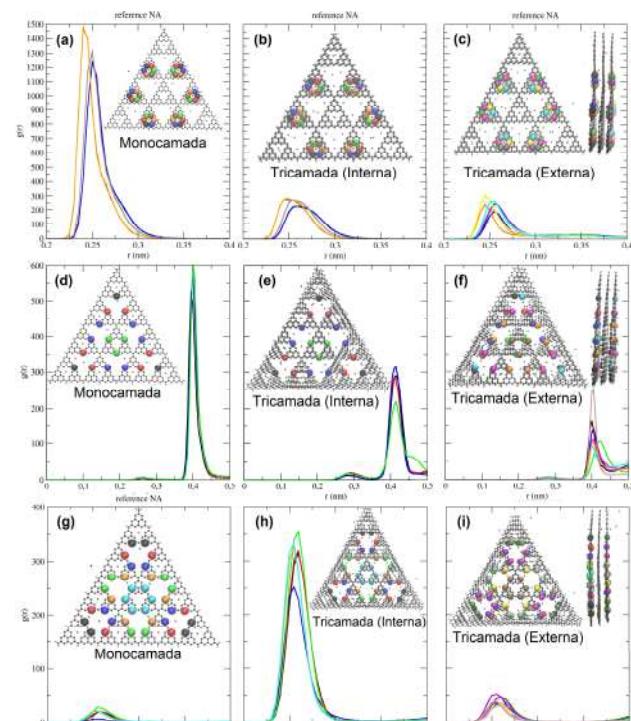


Figura 1: Distribuição radial de pares do Na^+ em relação aos N do poro menor (a), (b) e (c), aos N do centro da aresta (b), (e) e (h), e próximos ao vértice do poro maior (c), (f) e (i), respectivamente, para a monocamada, camada interna e camada externa do sistema com 3 camadas. As cores de cada curva correspondem às cores dos átomos selecionados nas estruturas desenhadas.

Conclusão

A análise das RDFs constatou que o Na^+ tende a permanecer nos poros menores tanto na monocamada quanto nas estruturas com mais camadas. E à medida que o número de camadas aumenta, ocorre um confinamento de Na^+ no poro maior, onde eles permanecem próximos ao vértice do poro, pois neste modo eles se coordenam com mais átomos.

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Dock2ONIOM: Utilitário Python para Rescoring de Poses de Docking Molecular pelo Método ONIOM.

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Palavras-Chave: *Docking Molecular, ONIOM, Python.*

Docking molecular é uma abordagem utilizada para predição das posições e orientações mais favoráveis de moléculas no sítio de ligação de um receptor.^[1,2] Esse processo utiliza um algoritmo de busca, que realiza uma amostragem do espaço conformacional, e o ranqueamento das poses obtidas com base em funções de scoring (estimativas de afinidades de ligação).^[2,3] No entanto, de forma geral, os scores obtidos em estudos de docking apresentam pouca correlação com afinidades de ligação experimentais,^[1,4] diminuindo a capacidade preditiva dessa abordagem.^[2,4] Uma das formas de melhorar tal questão é através do uso de energias baseadas em métodos de estrutura eletrônica para rescoring das poses de docking. Métodos de estrutura eletrônica são capazes de fornecer energias confiáveis, porém, possuem um custo computacional muitas vezes proibitivo para sistemas grandes e complexos.^[5] Uma das estratégias para contornar essa limitação é o uso de métodos híbridos, como o Our own N-layered Integrated molecular Orbital and molecular Mechanics (ONIOM).^[5] Esse método é baseado em um esquema extrapolativo em que o sistema real é dividido em camadas (sistema real e sistema(s) modelo(s)) e sua energia total é estimada utilizando-se cálculos de diferentes níveis de teoria nessas camadas.^[5] Nos cálculos ONIOM são usualmente empregadas 2 ou 3 camadas, combinando métodos de estrutura eletrônica e mecânica molecular. A preparação de arquivos de input para ONIOM é trabalhosa e não trivial comparativamente a outros cálculos e, portanto, o desenvolvimento de um software para auxiliar e automatizar esse processo é de grande relevância (Figura 1).

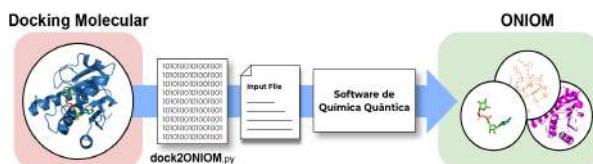


Figura 1 - Fluxograma do protocolo de docking rescoring com o método ONIOM usando o software Dock2ONIOM.

Dock2ONIOM está sendo desenvolvido utilizando-se a linguagem python 3.8.0 e fazendo uso de recursos do software PyMol.^[6] A primeira etapa do processo é a divisão do sistema em 2 (sistema real e sítio de ligação + ligante) ou 3 (sistema real, sítio de ligação + ligante e ligante) camadas, de acordo com a necessidade do usuário. O sítio de ligação é definido pelos átomos do sistema que estão a uma distância “r”, fornecida pelo usuário, do centro geométrico da molécula ligante e, no caso de proteínas, a seleção é feita com base em resíduos, de modo a manter seus átomos em uma mesma camada. O número de átomos de hidrogênio é corrigido e são determinadas as coordenadas dos link atoms. Na sequência, a multiplicidade de spin e a carga total de cada uma das camadas são calculadas, essa última propriedade utilizando-se cargas do tipo Gasteiger-Marsili do software OpenBabel.^[7,8] Para proteínas, há a opção de determinação do estado de protonação preferencial no pH especificado, também com recursos do OpenBabel.^[7,8] Após a determinação de todas essas informações, Dock2ONIOM gera arquivos de input completos para o cálculo ONIOM em softwares de estrutura eletrônica que suportam essa metodologia. O software Dock2ONIOM visa facilitar e automatizar a inclusão de métodos de estrutura eletrônica, através do método ONIOM, em estudos de docking molecular, melhorando o desempenho desta abordagem.

AGRADECIMENTOS: CNPq, FAPESP, CCES, IQ/UNICAMP.

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8 a 12 de Novembro de 2021

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Estabilidade na interação π - π em Moléculas de Cafeína em Solução Aquosa.

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Palavras-Chave: *Cafeína, simulação, solução.*

Introdução

A cafeína (1,3,7-trimetixantina) é um composto químico classificado como alcalóide e pertencente ao grupo das xantinas. É um dos principais estimulantes e psicoativos mais consumidos no mundo e apresenta grande importância tanto para a indústria alimentícia quanto para a farmacêutica [1]. A formação de dímeros de cafeína foi observada em configurações paralelas e antiparalelas, onde as moléculas de cafeína são giradas em ângulos diferentes entre si[1]. Neste estudo, iremos apresentar resultados da energia de formação de dímeros em fase gasosa e em solução aquosa.

Metodologia

A geometria das moléculas de cafeína nas orientações paralela e antiparalela foi otimizada em xTB, B97, B3LYP em nível de teoria conforme implementado no Orca [2]. As estruturas geométricas, as densidades de carga e a energia dessas moléculas foram analisadas com o objetivo de verificar a estabilidade do sistema e obter os parâmetros iniciais para a simulação. A simulação do dímero foi realizada em água usando o método de Monte Carlo implementado no software Dice [3].

Resultados

No estágio inicial, a energia de formação foi calculada em fase gasosa através da otimização das estruturas do dímero e do monômero. Os resultados para a energia de formação em fase gasosa estão mostrados na tabela 1 e Figura 1. Os resultados de fase gasosa mostram que estes dímeros são estáveis e com uma energia da ordem de 20 kcal/mol.

Tabela 1: Energia de interação entre duas moléculas na estrutura paralela e antiparalela.

Modelo	Energia de ligação (kcal/mol) $\Delta E = (E_{\text{dímero}} - 2E_{\text{monômero}})$	
	paralela	antiparalela
xTB	18.33	19.94
B97/svp	19.18	20.43
B3lyp/svp	23.64	25.26

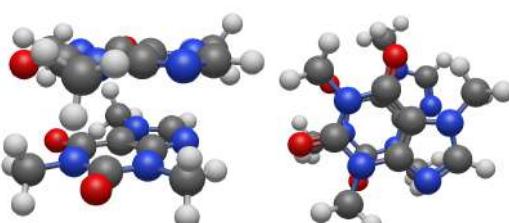


Figura 1: Estrutura do dímero otimizada.

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PREDICTING FIRST HYPERPOLARIZABILITY OF RUTHENIUM COMPLEXES WITH POTENTIAL TECHNOLOGICAL APPLICATION

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Palavras-Chave: *first hyperpolarizability; ruthenium complexes; basis set.*

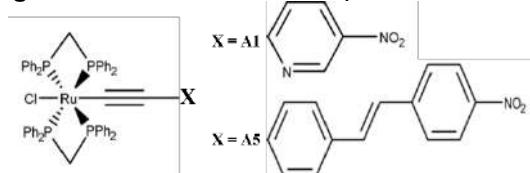
Introduction

Molecular materials with nonlinear optical properties (NLO) have been object of intensive studies due to their potential technological application. The experimental determination of these NLO properties is a difficult task and the quantum chemistry calculations have become a useful alternative for overcome this disadvantage and assist the experimentalists. However, NLO properties are strongly dependent of used theoretical approach^{1,2}. Thus, the present study aims to evaluate the influence of the DFT functionals and basis sets (Ru - RUBS/Ligands - LBS) for predicting first hyperpolarizability (β_t) of ruthenium (Ru) complexes with potential technological application.

Methodology

Initially, the ruthenium complex *trans*-[Ru(2-C≡CC₅H₃N-5-NO₂)Cl(dppm)₂], named as A1 (Figure 1), that presents experimental data for β available in the literature³, was chosen. The geometry of A1 complex was optimized and characterized as a minimum point on the potential energy surface through harmonic frequency calculations at B3LYP/def2-SVP/def2-SVP/IEF-PCM(UFF) level.

Figure 1. Structure of Ru complexes A1 and A5



Posteriorly, a set of 82 protocols using distinct DFT functionals and basis sets (RUBS/LBS) were used to assess the influence of the computational protocol for predicting β in A1 complex. Subsequently, β_t was calculated for A5 complex (Figure 1) using the protocols with the best results. The β tensor elements were calculated from the CPHF/CPKS method as implemented in the GAUSSIAN 09 program and the β_t property was obtained using the equation: $\beta_t = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$, where $\beta_i = \beta_{iii} + \sum_{i \neq j} (\beta_{ijj} + \beta_{iji} + \beta_{jji})$. The solvent effect was considered using the

IEF-PCM(UFF) approach. All calculations were performed in Gaussian 09 Rev. D. 01 program.

Results and Discussion

From obtained results, it was observed that RUBS do not have a significant influence for predicting β , while LBS have a fundamental role in predicting β . The analysis of DFT functionals showed that different functionals presented results with relative deviation around 10%. When A1 and A5 complexes are considered with the best protocols, the results (Table 1) showed a good agreement with the experimental values.

Table 1. Calculated β_t ($\times 10^{-30}$ esu) with the best computational protocols found in the present study.

Protocols	A1		A5	
	β_t	RD(%)	β_t	RD(%)
B3LYP/def2-SVP/def2-TZVP	465	2.6	2190	11.5
B3LYP/def2-SVP/jorge-DZP	443	5.4	1997	1.7
B3LYP/def2-SVP/jorge-TZP	474	1.2	2231	13.6
B3LYP/def2-TZVP/def2-TZVP	461	1.5	2163	10.1
B1B95/jorge-DZP/jorge-DZP	470	0.5	2026	3.2
B1B95/jorge-DZP/def2-TZVP	496	5.3	1886	4.0
Experimental ³	468		1964	

Conclusions

The study presented a sequential analysis of the role of the RUBS, LBS and DFT functional for predicting β_t of Ru complexes. The calculated results show that B1B95/jorge-DZP/jorge-DZP/IEF-PCM(UFF) is an excellent alternative for predicting first hyperpolarizability in Ru complexes.

Acknowledgments

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New methodology for thermal effects inclusion in 4f-4f intensity parameters based on vibrational normal modes

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Keywords: JOYSpectra, Thermal effects and Lanthanides

Introduction

The lanthanide ions (Ln^{n+}) formed in the complexation with ligands, present oxidation states +2, +3 and +4. One of the interesting points of these elements is precisely the incomplete 4f layer, which in turn suffers from the outermost layer shielding effects, decreasing the interaction of this layer with the ligand electrons, and decreasing the 4f-4f transitions.

In the Judd-Ofelt theory [1], the forced electric dipole and dynamic coupling mechanisms are responsible for explaining the 4f-4f transitions intensity parameters Ω_λ where ($\lambda = 2, 4$ and 6). The JOYSpectra software [2] has in its code the ability to solve the equations to obtain the Ω_λ , including the SOM (Simple Overlap Model) [3] and BOM (Bond Overlap Model) [4] approaches, where both consider the effects of covalence that are implemented in conjunction with the Judd-Ofelt mechanisms.

Although the temperature does not participate in the Judd-Ofelt expressions, thermal effects are responsible for geometric changes in the compound, in addition to activating vibration modes that can influence the energy transfer process. In this sense, to have computational models that include the thermal effects in the 4f-4f intensity parameters is paramount. Here is presented a computational implementation that allows the thermal inclusion in the Ω_λ using the normal vibrational modes.

Methodology

The new methodology was implemented in a development version of our JOYSpectra web platform [2]. After the implementation, a model system $[\text{Eu}(\text{H}_2\text{O})_8]^{3+}$ was used to perform the initial tests. The complex geometry optimization and frequency calculations were performed in Gaussian and Mopac programs, using the $\omega\text{B97XD}/\text{MWB52}/6-311++G(\text{d},\text{p})$ and PM6, respectively.

Results and discussion

The thermal corrected 4f-4f intensity parameters are written as follow:

$$\bar{\Omega}_\lambda = \sum_i^M p_i \Omega_{\lambda,i} \quad (1)$$

where p_i are the Boltzmann populations for different i geometry configuration, which can be generated using the Metropolis algorithm following the steps:

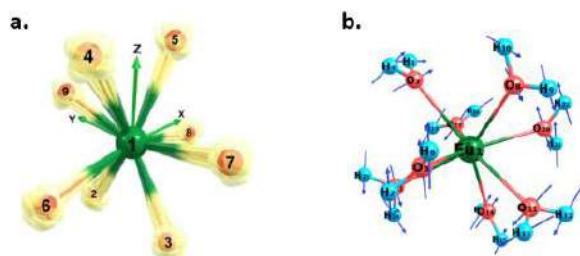
1. Generate a random atomic displacement dr_i ;
2. Generate the $P_i = \exp\left(\frac{-E_i}{k_b T}\right)$ probability from $E_i = k_j \cdot dr_i^2$. The E_i energy is obtained

considering the harmonic oscillator approach, where k_j are force constants from the frequency calculation and dr_i are the displacements;

3. Generate a random number $0 < t_i < 1$;
4. Test if $t_i \leq P_i$. If yes, the displacement dr_i and its energy are accepted.

This procedure allows the calculation of the 4f-4f intensity parameters considering all the vibrational modes calculated for a generic molecular system, taking into account i.e. more than 10^6 geometric configurations using Eq. (1) in minutes. Figure 1 shows the model system, including the mesh of ligating atom positions (Figure 1a) and the vibrational modes directions for a selected mode (Figure 1b).

Figura 1. EuCl_6 used for the CV model and $[\text{Eu}(\text{H}_2\text{O})_8]^{3+}$ is used for the MNV model.



In $T = 300$ K, an increase in the intensity parameters values is observed, where the most significant variation occurs in Ω_2 , being a consequence of its sensitivity to structural changes in the geometry. Also, the $\bar{\Omega}_2$ of our new methodology is in agreement with our Bose-Einstein based method⁵, that do not takes into account the population of each geometric configuration.

Conclusions

The thermal effects inclusion using normal modes is promising, giving results compatible with the literature. We are applying the methodology for other systems and making a comprehensive assessment of methodologies.

Acknowledgment

This work was funded by the Public Call n. 03 *Produtividade em Pesquisa* PROPESQ/PRPG/UFPB project number PVN13305-2020. The authors also thank the PPGQ-UEPB, CAPES, and CNPq institutions for their support.

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Computational Insights into Reaction Pathways for Chlorpyrifos and Chlorpyrifos-Methyl Toward Singlet Oxygen

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Keywords: Chemical reactivity, organophosphorus pesticides, density functional theory.

INTRODUCTION

In addition to our proposal for the OH-initiated unimolecular decomposition (**1**) of chlorpyrifos and chlorpyrifos-methyl – generally referred to as CLP – in the gas phase,¹ we present herein density functional theory (DFT) insights into the gas-phase reaction of the corresponding OH-initiated intermediates with singlet oxygen (**2**), and the direct reaction of the pesticides with singlet oxygen (**3**). This adds to what has been discovered so far.¹⁻³

METHODS

DFT calculations at PBE0-D3(BJ)/def2-TZVP and PWPPB95-D3(BJ)/def2-TZVP//PBE0-D3(BJ)/def2-TZVP levels were used to obtain free-energy surfaces. Rate constants were estimated by means of transition state theory (TST). Static correlation was treated by the double-hybrid functional level. Theoretical justification can be found in the literature.⁴

RESULTS

Reaction Mechanism in the Troposphere

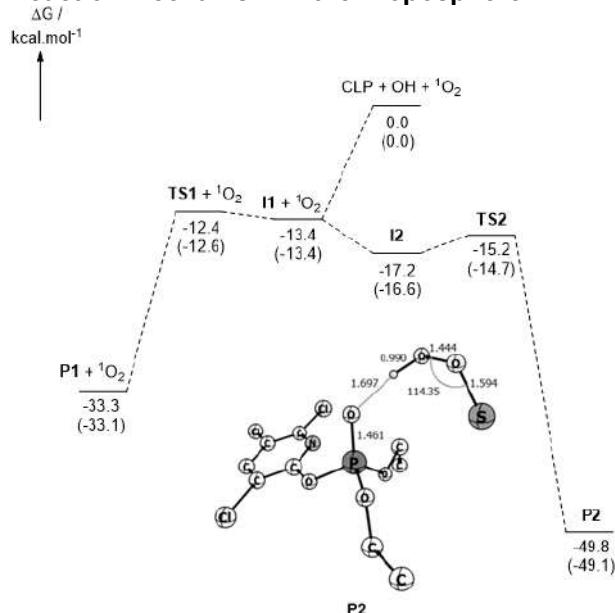


Figure 1: PBE0-D3(BJ)/def2-TZVP free-energy surface for the proposed mechanism in the troposphere. Values in parentheses describe chlorpyrifos-methyl reaction pathways. The plus sign indicates infinite separation.

Free-energy barriers at the PWPPB95-D3(BJ)/def2-TZVP//PBE0-D3(BJ)/def2-TZVP level yielded rate constant estimates for chlorpyrifos and chlorpyrifos-methyl (at 298.15 K and 1 atm) one order of magnitude faster than the measured values.^{2,3}

Direct Side-on Attack: Cyclic Intermediate?

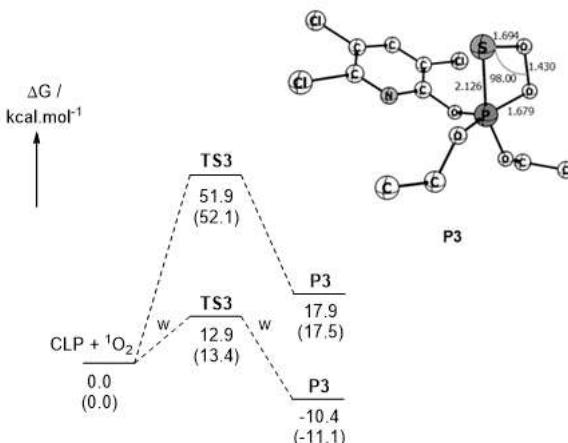


Figure 2: PBE0-D3(BJ)/def2-TZVP free-energy surface for the CLP + ${}^1\text{O}_2$ reaction. Values in parentheses are associated with chlorpyrifos-methyl. The label "w" indicates where water effects were included using the conductor-like polarizable continuum model (CPCM). Again, the plus sign indicates infinite separation.

At PWPPB95-D3(BJ)/def2-TZVP//PBE0-D3(BJ)/def2-TZVP, CPCM values for free energy of activation and reaction were 18.2 (18.6) and -7.1 (-7.7) kcal.mol⁻¹, respectively.

CONCLUSION

The global decomposition mechanism in the troposphere has been put forward for chlorpyrifos and chlorpyrifos-methyl. Moreover, the novel reaction pathway for the direct attack of singlet oxygen opens a venue to be explored by experimentalists.

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Estudo das propriedades eletrônicas e dos espectros de UV-VIS dos complexos de rutênio-areno

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Palavras-Chave: Rutênio-areno, complexos, DFT.

INTRODUÇÃO

Os complexos de rutênio-areno têm-se apresentado como uma opção à cisplatina no tratamento do câncer, por possuírem uma cinética de troca de ligantes semelhante, e por possuírem uma capacidade de transporte por importantes alvos biológicos como transferrina e a albumina¹⁻⁵. Portanto, o objetivo deste estudo é o de contribuir para a caracterização das propriedades eletrônicas utilizando a Teoria do Funcional da Densidade (DFT) e na caracterização das transições eletrônicas no espectro de UV/Vis de cinco complexos organometálicos de rutênio-areno que apresentaram boas atividade de biológicas. Os cinco complexos foram caracterizados experimentalmente, mas até o momento estudos químico quânticos não foram realizados: **1¹, 2², 3³, 4⁴, 5⁵**.

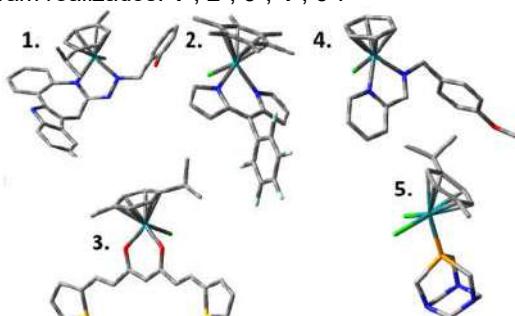


Figura 1 – Estrutura química dos complexos de rutênio-areno avaliados neste trabalho. Para melhor clareza, os átomos de hidrogênio foram removidos nas estruturas otimizadas.

METODOLOGIA

Os cálculos foram realizados com o funcional Perdew-Burke-Ernzerhof-Adamo (PBE0). A função de base def2-TZVP-PP foi aplicada para o rutênio, enquanto a 6-31G(d,p) foi utilizado para os demais átomos. Para simular o solvente foi empregado o método IEF-PCM. Todos os cálculos foram realizados pelo programa Gaussian 09.

RESULTADOS

Comparando as estruturas determinadas experimentalmente por difração de raio-X e a geometria calculada com o funcional PBE0, observamos um erro médio absoluto máximo para os comprimentos de ligações, ângulos e ângulos diedros de 0,07 Å, 2.8° e 87.9°, respectivamente. Os orbitais de fronteira HOMO e LUMO dos complexos

2 e **5** são majoritariamente compostos por orbitais-*d* do rutênio [d(Ru) e d(Ru)*]. Por outro lado, no caso dos complexos **1**, **3** e **4** observamos que o HOMO e LUMO são governados pelos orbitais π e π-antiligante (π*), respectivamente. Desta forma, os complexos **2** e **5** apresentam uma maior estabilidade cinética e uma menor reatividade em relação as demais, com base na diferença de energia HOMO-LUMO. Para avaliar a reatividade, parâmetros de reatividade baseado nas energias dos orbitais também foram analisados. Calculando o mapa do potencial eletrostático dos complexos de rutênio, observamos uma grande região de carga positiva na esfera de coordenação dos complexos, mas com uma área de carga negativa no ligante η⁶-areno localizada restritamente região externa do mapa. Já as estruturas **2** e **3** apresentam também uma grande região de carga negativa nos ligantes. Examinando os resultados experimentais do espectro de UV-Vis do complexo **1**, observa-se uma banda intensa em 316nm caracterizada majoritariamente por transições π→π* com base nos cálculos TD-DFT. No caso da estrutura **3**, a banda em ≈398nm se destaca por uma transição d(Ru)→π*, sendo o mesmo observado no complexo **4** na banda em ≈350nm. Já a banda larga em 342nm do complexo **5** é caracterizada por transições d(Ru)→d(Ru)* e π→d(Ru)*, similarmente ao complexo **2** na banda em 453nm. Já as transições π→d(Ru)* representam a natureza das bandas em 306nm e 513nm do complexo **2**.

CONCLUSÃO

Os resultados obtidos demonstraram que o funcional PBE0 utilizado pode ser aplicada com sucesso para elucidar geometria das estruturas, as propriedades eletrônicas e o espectro de UV/Vis experimental.

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Estudo teórico da adsorção dos pesticidas glifosato e DDT em IRMOFs

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Palavras-Chave: Adsorção, Metal Organic Framework, Pesticidas.

Introdução

Pesticidas são classificados como substâncias ou mistura de substâncias usada para o controle de alguma peste. Sua aplicação gera muitos resíduos que podem contaminar o solo e águas, bem como a sua continua ingestão pode provocar problemas neurais, câncer e outros¹.

Formas de remover pesticidas já presentes no ambiente, vem sendo exploradas, e neste contexto, materiais porosos como MOFs (*Metal Organic Frameworks*) são muito promissores devido a sua grande variedade de poros e área superficial que podem viabilizar a adsorção de grandes quantidades de determinadas moléculas².

Estudos envolvendo simulações computacionais, podem viabilizar informações importantes com potencial de direcionar escolha de uma ou mais MOFs para captura de um pesticida. Assim, neste estudo, a adsorção de glifosato e diclorodifeniltricloroetano (DDT) nas IRMOF-1, 8, 10 e 16 foi avaliada.

Metodologia

A partir das estruturas cristalográficas das IRMOF-1, 8, 10 e 16 obtidas no CCDC (*Cambridge Crystallographic Data Center*), foram geradas células primitivas, e suas geometrias de equilíbrio foram calculadas com condições periódicas utilizando DFT com pseudopotenciais GGA e o funcional PBE no programa VASP.

As MOFs calculadas foram utilizadas nas simulações de Monte Carlo Grã Canônico (MCGC), e tratadas com o campo de força GenericMOF contido no programa RASPA. Para os pesticidas, o *Universal Force Field* (UFF), foi utilizado. Durante a simulação a MOF foi mantida fixa, já os pesticidas foram limitados a liberdade em seus modos translacionais e rotacionais. A mistura de parâmetros foi feita utilizando Lorentz-Berthelot a partir dos parâmetros de Lennard-Jones dos campos de força citados.

Resultados

Os valores de adsorção obtidas a partir da simulação de MCGC podem ser observados na Tabela 1.

Tabela 1. Adsorção de glifosato e DDT.

MOF	Volume de poro (Å ³)	Adsorção (mg/g)	
		Glifosato	DDT
IRMOF-1	15184,39	1158,06	158,27
IRMOF-8	22394,38	1376,04	141,70
IRMOF-10	34748,03	2120,69	108,45
IRMOF-16	72403,77	3819,38	96,09

Os resultados mostraram que, para o glifosato, existe uma relação direta entre a adsorção e o volume de poro das IRMOFs com $R^2=0,995$, enquanto, para o DDT essa relação crescente não foi observada.

Para o glifosato, foi observado que as moléculas interagem com o poro das IRMOFs e entre elas de forma eficiente, apresentando ligações de hidrogênio como a interação mais presente, o qual contribuiu para uma relação direta entre volume do poro e a adsorção. Apesar das moléculas de DDT interagirem com eficiência com as IRMOFs, a interação entre moléculas de DDT é desfavorecida.

Também foi visto que, a interação entre o DDT e as IRMOFs é regida preferencialmente por forças de van der Waals, bem como, a interação entre moléculas de DDT que estão contidas nos poros da IRMOF-1 e IRMOF-8. Com o aumento do volume do poro a contribuição por Coulomb com caráter repulsivo passa a ser cada vez mais dominante na interação entre moléculas de DDT, e essa interação por Coulomb (repulsivo) contribui para a menor adsorção da IRMOF-16, adsorção essa que passa a ser limitada a regiões próximas a unidade inorgânica desta IRMOF.

Conclusões

Por meio de simulação computacional, foi possível observar que existe uma relação direta entre volume de poro e a adsorção de glifosato nas IRMOFs, e essa interação entre moléculas de glifosato tem forte papel nessa observação. Para moléculas de DDT, a repulsão entre elas provoca uma queda gradativa na adsorção, que para a IRMOF-16 está limitada a interação com a unidade inorgânica desta.

Por fim, a IRMOF-16 tem maior potencial para aplicações com foco na captura de glifosato e a IRMOF-1 para o DDT.

Agradecimentos

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Analyzing the Trans Effect in Pt(II) Complexes from the Overlap Model Perspective

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Keywords: *Trans effect, Pt(II) complexes, Overlap Model, DFT.*

INTRODUCTION

The ligand exchange reactions in square-planar Pt(II) complexes represents one of the most well-established reaction mechanism in inorganic chemistry,^{1,2} where features like stereochemistry of generated products as well as the activity of these compounds usually can be rationalized based on concepts of the trans influence (bond lengths, vibrational frequencies, magnetic resonance parameters, thermodynamics) and trans effects (kinetic, activation energies, rates of substitutions reactions). Despite the well-accepted interpretation of the trans effect from kinetics measures, in order to get complete comprehension about it, is crucial to try to understand the chemical nature of the Metal-Ligand interaction along to full reaction coordinate, evaluating at each point the contribution of both spectator and “actor” ligands. Thus, in this work, we have applied Density Functional Theory and the recently developed chemical bond overlap model³ (OP model) in order to propose a new interpretation for the trans effect in *trans*-Pt(NH₃)₂(H₂O)T (T=F, Cl, Br, CO, CN, NO) complexes in solution.

METHODOLOGY

Full unconstrained geometry optimization and frequency calculations were carried out at the BP86/SBKJC(Pt)/cc-PVQZ(ligands)/PCM level of theory. All structures were characterized as true minima or first-order transition states by determination of the harmonic frequencies. The reaction pathway was analyzed from IRC calculations starting from the respective transition states. From the characterized intermediates and transition states, the overlap properties (electron density, Intra-overlap repulsion energy J_{OP}^{intra}) were calculated using the homemade ChemBOS software.

RESULTS

The J_{OP}^{intra} quantify the Coulomb repulsion of the overlap density and itself, carrying information about its compacity degree, as well the density concentration in the bond region. Fig. 1 a) and b), present the variation of J_{OP}^{intra} along the reaction coordinate for the H₂O exchange reaction in the *trans*-Pt(NH₃)₂(H₂O)T (T=F⁻, CN⁻) complexes.

As shown in Fig. 1a (with T=F⁻), following the H₂O substitution reaction, the value for the Pt – O bond for

the leaving water molecule vanishes while increasing for the arriving group.

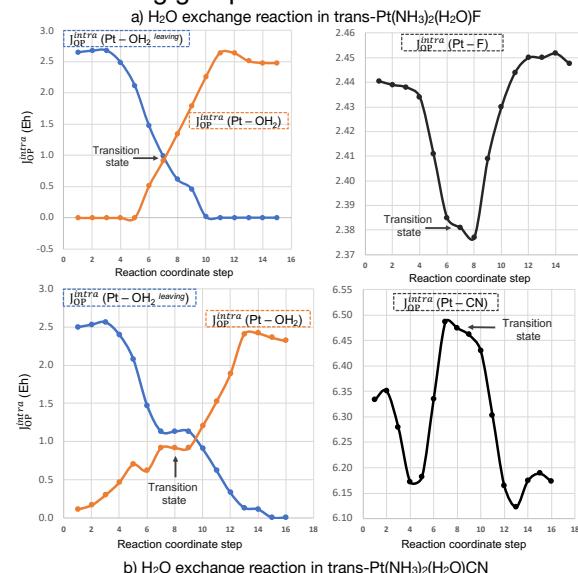


Fig. 1: Intra-overlap repulsion energy (in Eh) for (a) Pt – O and Pt – F bonds, and (b) Pt-O and Pt-CN bonds.

It is also observed for the water substitution in *trans*-Pt(NH₃)₂(H₂O)F that the value for Pt – F bond has a local minimum near to the TS, indicating that, at this point, the spectator bond becomes more spread in space. Concerning the reaction in *trans*-Pt(NH₃)₂(H₂O)CN, the behavior along the reaction coordinate is the opposite to observed with F⁻. As shown in Fig 1 b), the formation of the TS is accomplished by a local maximum, which means that the electron density of the Pt-CN bond in this region is more concentrated concerning reactant. Contrary to the observed reaction with F⁻, the result for CN⁻ indicate that the Pt-CN bond at the TS assumes the most strong covalent character during the reaction. Overall, our results indicate that this strong covalent character at the TS is correlated with the more substantial trans effect of π-ligands as CN⁻, CO, and NO.

ACKNOWLEDGMENTS

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PREDICTING Pt-195 NMR CHEMICAL SHIFT IN Pt(II)-Sn(II) COMPLEXES WITH POTENTIAL CATALYSTIC APPLICATION

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Palavras-Chave: Catalyst, Pt(II)-Sn(II) complexes, NMR.

Introduction

The Pt(II)-Sn(II) complexes are known as excellent homogeneous catalysts and they have been very useful, having more advantages than the industrial catalysts. Although the solid structures for many complexes are known, identifying these complexes in solution has been a challenge¹. In this context, the NMR spectroscopy is an excellent alternative for the characterization of these complexes in solution¹ and the Computational Chemistry can aid in the interpretation of NMR spectra². However, the theoretical prediction of NMR parameters in Pt(II)-Sn(II) complexes is not a trivial technique due to the presence of heavy metals, where the inclusion of relativistic effects is of great importance². So, in the present study, a computational protocol developed by Paschoal et al.² for predicting Pt-195 NMR chemical shift in Pt(II) complexes was applied in the study of Pt(II)-Sn(II) complexes..

Methodology

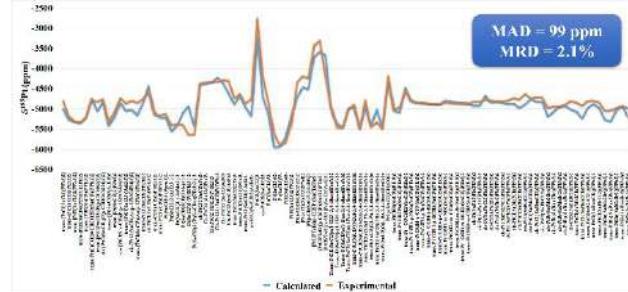
Initially, a set of 100 Pt(II)-Sn(II), that have NMR experimental data available in the literature, were selected. The structure of each complex was optimized and characterized as a minimum point on the potential energy surface at B3LYP/LANL2DZ/def2-SVP/IEF-PCM(UFF) level. The Pt-195 NMR chemical shift ($\delta^{195}\text{Pt}$) was calculated using the empirical equation model²: $\delta^{195}\text{Pt}_{\text{calc}} = -0.9250 \times {}^{195}\sigma_{\text{calc}} - 2065.7558$, where the shielding constant (σ) was calculated at the GIAO-PBE/NMR-DKH/IEF-PCM(UFF) level. All calculations were carried out using GAUSSIAN 09 program Rev. D.01.

Results and Discussion

The calculated $\delta^{195}\text{Pt}$ for the 100 Pt(II)-Sn(II) complexes studied are displayed in Fig. 1. From the calculated values, we can observe that the calculated values with the empirical equation model presented a good agreement with the experimental values, with a mean absolute deviation (MAD) and a mean relative

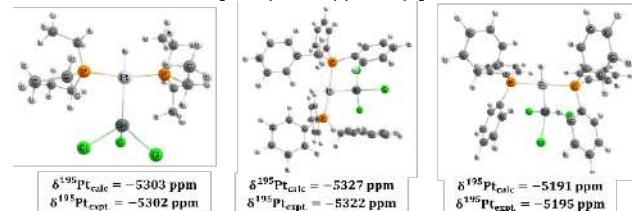
deviation (MRD) 99 ppm and 2.1%, respectively, and a R^2 of 0.8581.

Fig. 1. Calculated and experimental $\delta^{195}\text{Pt}$ for the 101 Pt(II)-Sn(II) complexes studied.



From Fig. 2, it can be observed that the computational model is able to distinguish with very small variations in $\delta^{195}\text{Pt}$, which indicates that the model has a high sensitivity.

Fig. 2. Calculated $\delta^{195}\text{Pt}$ for the *trans*-[PtH(SnCl₃)₂(PEt₃)₂], *trans*-[PtH(SnCl₃)(PPh₂CH₂Ph)₃] and *trans*-[PtH(SnCl₃)(PPh₃)₂].



Conclusions

The study presented an application of computational protocol for predicting Pt-195 NMR chemical shift in Pt(II)-Sn(II) complexes. The calculated results showed that the proposed model is an excellent alternative to assist in the predicting the NMR chemical shift.

Acknowledgments

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Experimental and computational study of new deep eutectic solvents based on Benzalkonium chloride

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Keywords: infrared, DES, characterization.

Introduction

Deep eutectic solvents (DES) are green solvents with a low melting point, often formed by a salt and a hydrogen bond donor (HBD). DES has different advantages, such as low-cost materials with greater availability and low toxicity.¹ Recently, some authors have used experimental methods associated with computational methods to investigate the structural properties and intermolecular nonbonding interactions in DES.² In this context, the objective of this work is to report the synthesis and characterization of 3 new benzalkonium based-DES, through experimental and computational vibrational spectroscopy.

Methodology

The new systems are composed of the combination of benzalkonium chloride (BzkCl, Figure 1a) with three different types of hydrogen bond donors: glycerol (Gly, Figure 1b), oxalic acid (AcOx, Figure 1c), and citric acid (AcCit, Figure 1d). DES ([BzkCl]: Gly], Figure 1e) ([BzkCl]: AcCit], Figure 1f) and ([BzkCl]: AcOx], Figure 1g) were prepared from a 1:1 molar ratio, heated at 100°C (oil bath) and stirred until the formation of a viscous and homogeneous liquid.

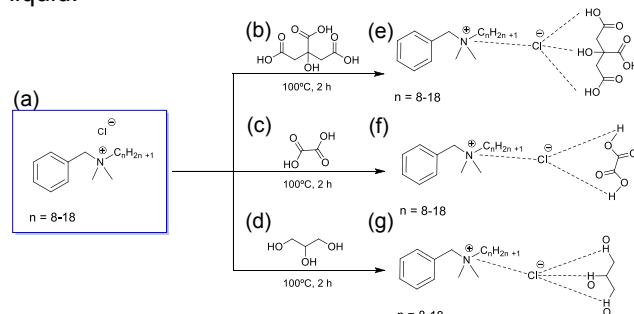


Figure 1. Structures and synthetic routes of DES from Benzalkonium chloride and an equivalent of the respective HBDs.

The geometry optimizations and vibrational frequencies were performed for different conformations at the CAM-B3LYP/6-311++g(d,p) theory level in the Gaussian16 program. Infrared analyzes were performed on an Agilent Cary 630 FTIR benchtop spectrometer, using the ATR technique, in the range of 4,000 to 650 cm⁻¹. Eight scans were performed for each sample with a resolution of 4 cm⁻¹.

Results and discussion

The experimental and theoretical infrared spectra of the studied DES are shown in Figure 2. From this

figure, we can observe broad and strong bands in the range between 3600 and 3100 cm⁻¹ corresponding to -OH vibration stretching and the formation of hydrogen bonds, which are a characteristic of DES formation.³ On the other hand, the band shape can vary in function of the presence of moisture, which can only be observed in the FTIR experimental results.⁴

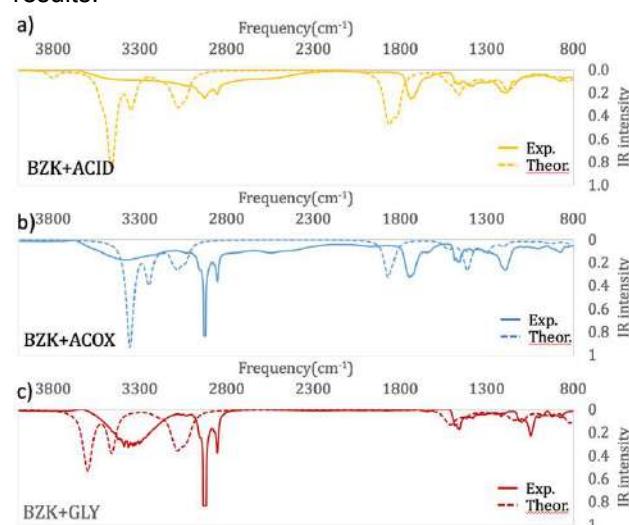


Figure 2. Combined calculated and experimental spectra

In the experimental and theoretical spectra, the carbonyl bands in [BzkCl:AcCit] and [BzkCl:AcOx] are observed in the region of 1700 - 1800 cm⁻¹. The theoretical results corroborate the peak attribution. It is important to highlight that the theoretical vibrational spectra are in good agreement with the experimental data, given that the systems were calculated without the inclusion of extended effects, and for only one conformation.

Conclusion

Experimental and theoretical infrared data agree and are powerful tools to elucidate benzalkonium based DES structure.

Acknowledgments

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Estudo das propriedades estruturais e eletroquímicas *in silico* de β -FeOOH

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Palavras-Chave: Reatividade química, Akaganeita, Potencial redox.

INTRODUÇÃO

O sistema $\text{Fe}_{7,6}\text{Ni}_{0,4}\text{O}_{6,35}(\text{OH})_{9,65}\text{Cl}_{1,25}$ possui ocupação atômica fracionada, pertence ao grupo espacial I_2/m , e suas ligações do ambiente octaédrico FeO_6 são distorcidas, com comprimentos $\text{Fe} \dots (\text{O}, \text{OH})$ variando de 1,94 a 2,13 Å^[1, 2]. Com base nas características brevemente apresentadas, nos dados cristalográficos da akaganeita obtidos no banco de dados^[3], e em função da ocupação fracionada característica do sistema - que dificulta um estudo *ab initio* - elaboramos um modelo computacional do mineral a partir da fórmula estequiométrica $\text{Fe}_8\text{O}_8(\text{OH})_8 \cdot 2\text{HCl}$, vislumbrando minimizar desordens causadas pela ocupação fracionada.

Investigamos *in silico* as propriedades estruturais, eletrônicas e eletroquímicas da Akaganeita. Estudamos a reação catódica do sistema através da inserção de íons Li^+ na cavidade estrutural da akaganeita, e estimamos o potencial de oxirredução do complexo $\beta\text{-FeOOH}/\text{Li}$ em -1,0V.

METODOLOGIA

DFT/ondas planas foi utilizada no estudo do *bulk* da akaganeita, por meio do pacote computacional *Quantum Espresso*^[4]. Usamos o funcional XC GGA/PW91, pseudopotencial *ultrasoft*, malha de pontos k 2x2x4, raio de corte 60Ry. Sistema de spin compensado antiferromagnético, convergência de 10^{-6} Ry. Para estimar o potencial de oxirredução da akaganeita contendo íons Li^+ na estrutura de cavidade, a geometria do $\beta\text{-FeOOH}$ foi completamente otimizada utilizando o método BFGS^[5]. Para a estimativa do potencial eletroquímico do processo de oxirredução (Eredox), considerando o íon Li^+ no interior da cavidade presente na estrutura da akaganeita, fizemos a aproximação $\Delta G_{\text{total}} \approx \Delta E_{\text{cátodo}}$, nesse caso $\beta\text{-FeOOH}$ sem o íon, utilizando a equação de Nernst para calcular a energia livre total do processo redox (Eq. 1).

$$\Delta G_{\text{redox}} = -F E_{\text{redox}} = \Delta G_{\text{cátodo}} - \Delta G_{\text{anodo}}$$

RESULTADOS

Tabela 1: Valores de comprimento de ligações de $\beta\text{-FeOOH}$ calculados.

Referências	Comprimento de ligação* (Å)				
	Fe-OH (1)	Fe-OH (2)	Fe-O (1)	Fe-O (2)	H-Cl
Experimental					
Post e Buchwald ^[1]	2,14	2,06	1,92	2,04	1,70
Post <i>et al.</i> ^[2]	2,05	2,04	1,95	1,99	2,22
Modelo (i) $\beta\text{-FeOOH-HCl}$					
Este trabalho					
GGA/PBE/US	2,09	2,12	2,13	1,95	2,11
GGA/PW91/US	2,09	2,11	2,13	1,95	2,12
LDA/PZ/US	2,03	2,07	2,03	1,90	2,01
Experimental					
Post e Buchwald ^[1]	2,14	2,06	1,92	2,04	-
Post <i>et al.</i> ^[2]	2,05	2,04	1,95	1,99	-
Modelo (ii) $\beta\text{-FeOOH}$					
Este trabalho					
GGA/PBE/US	2,19	2,15	1,88	1,96	-
GGA/PW91/US	2,18	2,14	1,88	1,96	-
LDA/PZ/US	2,09	2,08	1,81	1,90	-

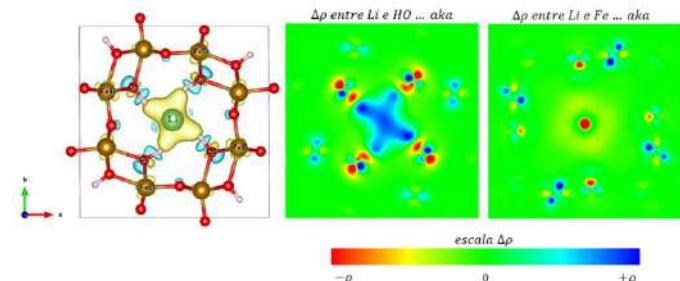


Figura 1. Diferença de densidade eletrônica ($\Delta\rho$) do sistema contendo um íon Li^+ na cavidade da akaganeita.

CONCLUSÕES

Cálculos DFT/ondas planas foram realizados para uma descrição adequada de propriedades estruturais do *bulk*, e mostraram boa concordância dos modelos elaborados neste trabalho com os parâmetros cristalográficos experimentais. Do ponto de vista eletroquímico, a inserção de íons Li^+ na estrutura da akaganeita nos permitiu estudar a reação catódica, mostrando que o Li sofre oxidação, promovendo elétrons através da redução dos sítios de Fe presentes em $\beta\text{-FeOOH}$.

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Linear mapping between magnetic susceptibility and entanglement in conventional and exotic one-dimensional superfluids

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Palavras-Chave: *Entanglement, Magnetic Susceptibility, Superfluids.*

Introduction

Entanglement has been proved to be an excellent parameter for detecting quantum phase transitions and also for characterizing quantum many-body states, including exotic states of matter. Entanglement has also played a central role in bridging quantum information theory to different areas, as condensed-matter, high-energy, and cold-atom physics. We investigate the ground-state entanglement of the single-band one-dimensional Hubbard model at zero temperature and its connection to the magnetic susceptibility. Our analysis reveals that the mapping between entanglement and magnetic susceptibility in conventional and exotic superfluids; is surprisingly simple: directly proportional. This demonstrates not only that there are an intrinsic relationship between the quantities, but specially that entanglement could be quantified via the measurement of magnetic susceptibility in current cold atoms experiments.

Methodology

The Hubbard hamiltonian is described by hopping, interaction and external potential terms respectively:

$$\hat{H} = - \sum_{ij\sigma} t_{ij} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_{i\sigma}) + \sum_i U_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \sum_{i\sigma} v_{i\sigma} \hat{n}_{i\sigma}$$

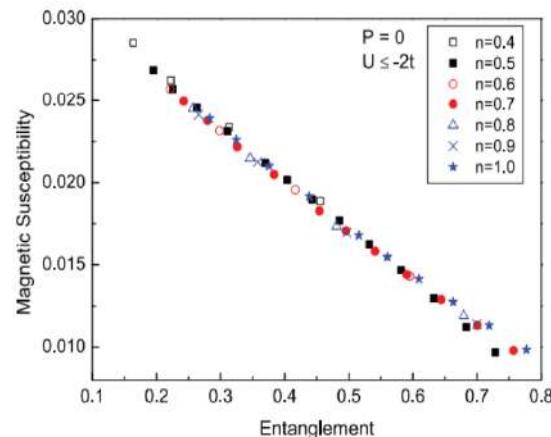
The magnetic susceptibility is related to the second derivative of the total energy, with respect to the magnetization, as

$$\chi^{-1} = \frac{\partial^2 E(n, m, U)}{\partial m^2}$$

Here the ground-state energy has been obtained with DMRG techniques.

Results

We find signatures of the metal-insulator transition and of the BCS-BEC crossover, but the most relevant result is that for conventional and exotic superfluids the mapping between magnetic susceptibility and entanglement is surprisingly simple: Directly proportional. This linear behavior is found to be universal for conventional superfluids and therefore could be exploited to quantify entanglement in current cold-atom and condensed-matter experiments.



Conclusion

By exploring a vast regime of interactions U, densities n, and polarizations P, thus comprising the metallic, insulating, conventional superfluid and exotic polarized (FFLO) superfluid phases, we found a surprising linear mapping between χ and S in conventional ($P = 0$) and exotic ($P < PC$) superfluids.

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Linear mapping between magnetic susceptibility and entanglement in conventional and exotic one-dimensional superfluids. D. Arisa and V. V. França, Phys. Rev. B 101, 214522 (2020).



PREDICTING Co-59 NMR CHEMICAL SHIFT USING THE NMR-DKH BASIS SETS

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Keywords: cobalt complexes, NMR, basis sets.

Introduction

The transition metals NMR is a useful tool for experimentalists. The Co-59 is an NMR active nucleus with the nuclear spin $I = 7/2$ and 100% of natural abundance. It is an important nucleus because it has ease of detectable NMR signals in both liquid and solid-state¹. The Co-59 NMR chemical shift ranges around 18,000 ppm, one of the largest known in NMR spectroscopy¹. Besides, Co-59 has a large quadrupole moment. It turns half-height line widths very sensitive to external electric field gradients in the nucleus neighborhood. Therefore, peaks can be broad². Furthermore, protocols to predict NMR chemical shifts for some metal nuclei are an important issue³. In the present contribution, we propose a new NMR-DKH basis set for the Co atom and a computational protocol (NMR//Structure) to predict the Co-59 NMR chemical shift ($\delta^{59}\text{Co}$) in Co(III) complexes.

Methodology

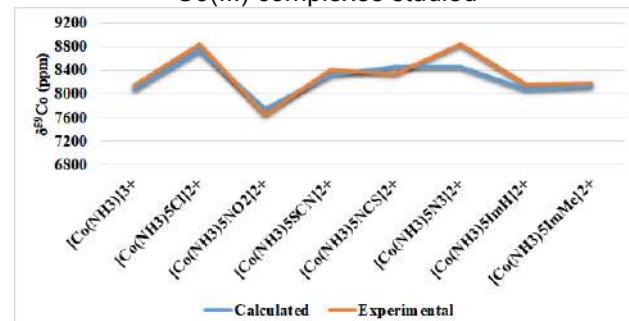
Computational protocols were built using a set of six Co(III) compounds. The geometries of complexes were optimized and characterized as stationary points on potential energy surface through harmonic frequency calculations. The solvent effect was included using the IEF-PCM(UFF) approach and NMR calculations were performed using the GIAO method. The protocols were constructed using a set of 12 DFT functionals (LOT), 5 basis sets for cobalt (COBS) and 3 for ligands (LBS). The $\delta^{59}\text{Co}$ was calculated according to equation: $\delta^{59}\text{Co} = \sigma_{ref} - \sigma_{calc}$, where σ_{ref} is the shielding constant for the internal reference, $[\text{Co}(\text{CN})_6]^{3-}$ in H_2O , and σ_{calc} is the shielding constant for the Co under consideration. All calculations were performed in Gaussian 09 Rev. D. 01 program.

Results and Discussion

From the calculated results, the BB95/LANL2DZ/jorge-DZP/IEF-PCM(UFF) level

presented the best relation between structure and Co-59 NMR chemical shift, with a mean relative deviation (MRD) of 1.41% for the structural parameters of the set of 6 Co(III) complexes used in the protocol development. For the $\delta^{59}\text{Co}$, the B3LYP/NMR-DKH/IEF-PCM(UFF) level presented the best description, with a mean absolute deviation (MAD) only of 99 ppm. Thus, the protocol was applied in a set of 9 Co(III) complexes (Fig. 1). The results showed a good agreement between calculated and experimental values, with a MAD and MRD of 127 ppm and 1.5%, respectively.

Fig. 1. Calculated and experimental $\delta^{59}\text{Co}$ for a set of 8 Co(III) complexes studied



Conclusions

The present study proposed a computational protocol to predict the structure and the Co-59 NMR chemical shift in Co(III) complexes. The final protocol, GIAO-B3LYP / NMR-DKH / IEF-PCM(UFF) // BB95 / LANL2DZ / jorge-DZP / IEF-PCM(UFF) presented a MRD only of 1.5% for a set of 8 studied Co(III) complexes.

Acknowledgments

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Crystallization solvents affect the intramolecular energy transfer rates in Eu(III) complex.

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Palavras-Chave: Lanthanide Spectroscopy, JOYSpectra , Intramolecular Energy Transfer.

Introduction

The absorption/emission photophysical properties of Lanthanide compounds are widely studied using chelate ligands. This type of ligand can affect the intramolecular energy transfer (IET) in lanthanide compounds due to its geometric constraints. Also, the presence of crystallization solvents can affect the IET. In this work, these issues are addressed for the 8-hydroxy quinoline complex with Eu³⁺ and Tb³⁺ ions.

Methodology

All molecular structures of the complexes were optimized using the DFT in Gaussian 16 software. The ωB97X-D/MWB52(Ln)/6-311++G(d,p)(ligands) level of theory was used. The excited states (T₁ and S₁) were obtained using the time-dependent density-functional theory approach (TD-DFT) using the same procedure described for the geometry. The IET calculations were done in our JOYSpectra web platform [1]

Results and discussion

From the TD-DFT calculations, the donor energy levels (S₁ and T₁) were obtained and their respective

donor-acceptor distances. Table 1 summarizes all the donor energy positions.

Table 1. Donor-acceptor distances R_L (in Å), S₁ and T₁ states (in cm⁻¹) obtained from TD-DFT.

Compound	R _L	S ₁	T ₁
[LnPYCyclen]	4.01	25688	17719
[LnPYCyclen](MeOH, H ₂ O)	4.04	28244	19380

Each excitation is composed of a few transitions between molecular orbitals (MOs) HOMO-X → LUMO+Y. Both S₁ and T₁ states are well-localized at the aromatic rings of the ligand while the NO₃⁻, CH₃OH, and H₂O do not participate directly in the S₁ and T₁ compositions. However, the increase of the S₁ and T₁ energy states when we compare the complexes with and without crystallized solvents can be interpreted as a significant structural change because of the presence of CH₃OH and H₂O molecules around, confining the electronic density in the ligand's aromatic rings.

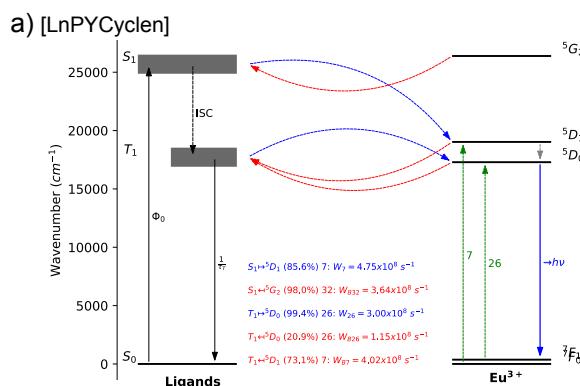
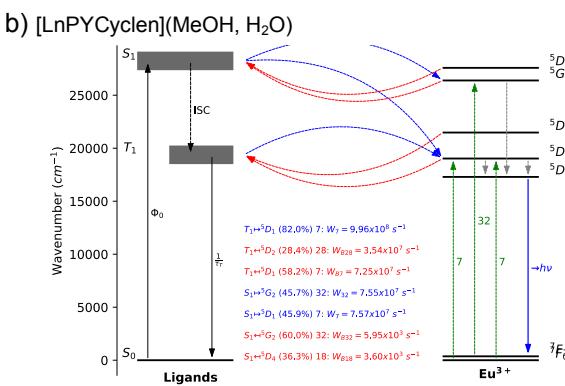


Figure 1. Schematic energy level diagrams for the Eu-based complexes considered in this work. The S₁ and T₁ states for compounds. (a) Free-solvent complex diagram. (b) Diagram for the complex with CH₃OH and H₂O molecules in the crystallographic structure.

The effect of the crystallization solvent (out of the coordination sphere) provided energy blue shifts of 1661 and 2556 cm⁻¹ for the T₁ and S₁ states, respectively. In Figure 1, the IET results indicate that the T₁ → Eu³⁺ is the most effective energy transfer channel for the two complexes, a scenario that is



visualized if the crystallization solvent is taken into account.

Acknowledgments

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Structural Modeling of Glycans: Improve Conformations Sampling

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Palavras-Chave: glycans molecules, nonpolar surface area, replica exchange molecular dynamics

INTRODUCTION

Proteins are usually modified by binding to glycans and it is estimated that more than half of human proteins are glycosylated. Changes in the glycosylation pattern have been associated with numerous diseases, such as Alzheimer's disease and Parkinson's disease. The analysis of glycans and glycoproteins is challenging due to the high complexity and structural microheterogeneity resulting mainly from various isomers. Even with combinations of advanced experimental techniques, they have difficulties in obtaining the correct structure of glycans. The increase of nonpolar surface area (NPSA) for these structures was successfully correlated to retention time from liquid chromatographic separations measurements.

Hence, accurate theoretical estimations of the structural microheterogeneity of glycan isomers were obtained using classical simulations, and submitted selected conformations to ab initio optimization. The selected systems are some samples of bi and tri-antennary glycans, as some examples table below.

Name	Glycans in SNFG representation
core	
Branch	
2,6	
2,3	

Table 1: The selected bi-antennary glycans used in this work.

METODOLOGY

The conformations were obtained with parallel simulations using replica exchange molecular dynamics (REMD). Classical simulation was performed with Gromacs package using General Amber Force Field (GAFF) and acetonitrile solvent.

Different conformations were selected by the root mean square deviation (RMSD), then submitted to an optimization performed with GEN2-xTB, always considering the solvent environment.

RESULTS

The number of conformations after the RMSD criteria is around 80 for each glycan. Some conformers compete for the lowest energy position and therefore an average using Boltzmann weight was employed (Boltzmann), and compared to the PBE/SV optimization (OPT/DFT). Also, the conformer with lowest energy (REMD/XTB) was compared. The main result is plotted in figure 1.

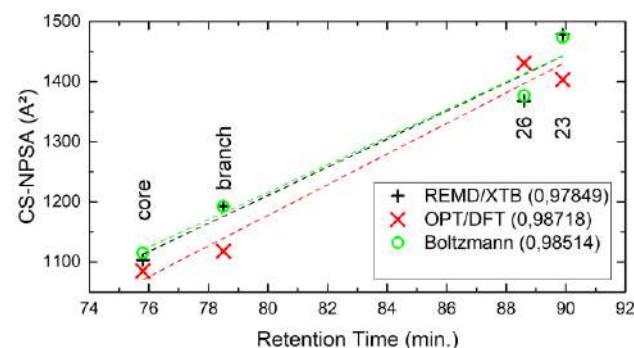


Figure 1: The correlation between calculated NPSA and experimental retention time. In parenthesis the Pearson's R value.

CONCLUSIONS

The bi-antennary system shows excellent correlation between NPSA and retention time using the REMD methodology. The result is independent of analyzing all the conformations obtained via RMSD or just the lowest energy. The great advantage of this new procedure is the computational time compared to an ab-initio optimization. The biggest challenge is to deal with the tri-antennary systems that have not presented good correlation with the experimental data so far.

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Relativistic Computational Study of Aquation Reaction of Cisplatin

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Palavras-Chave: *cisplatin, basis sets, relativistic effects.*

Introduction

In 1965, Barnett Rosenberg et al. discovered the cytotoxic properties of cisplatin [*cis*-diaminodichloroplatinum(II)] and, after being approved by the FDA in 1978, have been widely used in chemotherapy treatments. However, this compound has high toxicity and low selectivity which ends up causing several side effects. Thereby, new Pt(II) complexes have been studied in search of new compounds that have the advantageous characteristics of cisplatin and can overcome it in relation to its undesirable effects. Therefore, the aquation reaction of the Pt(II) complexes that occurs when the drug enters the cell should be analyzed to find molecules that have better antitumoral properties^{1,2}. In this context, the Computational Chemistry could help evaluating the geometries, electronic structures and the Gibbs free energy of activation for these complexes³. So, in the present study, we will study the reactivity of Pt(II) complexes in order to evaluate the influence of Pt basis set and relativistic effects in predicting the Gibbs free energy of activation for the ligand exchange reaction (Cl-/H₂O) of cisplatin.

The calculated results³, Table 1, indicate that for a good description of cisplatin reactivity, an ECP with a valence triple-zeta basis set or an all-electron Pt basis set with the inclusion of relativistic effects should be considered. Besides, the results suggest that there were no significant differences between the double- and triple-zeta basis set, so the choice of the Sapporo-DKH3-DZP-2012 is indicated as being less computationally costly.

Table 1. Gibbs free energy of activation (ΔG_a , kcal mol⁻¹) for some protocols studied.

B3LYP/Pt basis set/Ligands basis set	Error
def2-svp/Jorge-DZP	4.54%
def2-svp/cc-pVDZ	5.02%
def2-SVP/def2-SVP	0.06%
LANL2DZ/Jorge-DZP	8.59%
LANL2DZ/cc-pVDZ	5.10%
LANL2DZ/def2-SVP	3.27%
Sapporo-DKH3-DZP-2012/Jorge-DZP-DKH	1.70%
Sapporo-DKH3-DZP-2012/cc-pVDZ-DK	2.30%
Sapporo-DKH3-DZP-2012/DK-def2-SVP	10.08%
DZP-DKH/Jorge-DZP-DKH	4.49%
DZP-DKH/cc-pVDZ-DK	1.88%
DZP-DKH/DK-def2-SVP	1.90%
Pt-mDZP/Jorge-DZP	22.59%
Pt-mDZP/cc-pVDZ	0.83%
Pt-mDZP/def2-SVP	2.15%

Methodology

We studied the ligand exchange reaction (chlorine/water) of cisplatin using different computational protocols. Nonrelativistic and relativistic 2nd order Douglas-Kroll-Hess (DKH2) calculations were carried out at DFT level using the B3LYP functional. Effective core potentials (NR-ECP), nonrelativistic all-electron (NR-ABS), relativistic all-electron (REL-ABS) basis sets were used for Pt atom. For ligands, the jorge-DZP basis sets were used in NR calculations and jorge-DZP-DKH basis sets were used in DKH2 relativistic calculations. Furthermore, the implicit C-PCM solvation model, defining water as a solvent, was used to consider the solvent effects. The Gibbs free energy of activation of the reaction (ΔG_a) was calculated as $\Delta G_a = G(TS - G(I1))$. All calculations were performed using ORCA 4.2.1 program.

Conclusions

The present study presented an analysis of the role of the Pt basis set and relativistic effects in computational prediction of cisplatin reactivity. The results show that REL-ABS or NR-ECP with a valence triple-zeta basis set should be considered for an adequate description.

Acknowledgments

The authors would like to thank the Brazilian agencies CNPq, CAPES, FAPERJ and FAPEMIG.

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Results and Discussion



Does only size matter? Assessing the influence of functional groups on CO₂ capture by Covalent Organic Frameworks 2D

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Palavras-Chave: *gas capture, Covalent Organic Frameworks, GCMC calculations, DFT calculations*

Introduction

A class of materials that have attracted great interest recently is the Covalent Organic Frameworks (COFs), an emerging class of crystalline organic nanoporous materials designed in a bottom-up approach by the covalent bonding of one or more building blocks into extended reticular structures.^[1,2] Due to the atomic precision control that these materials present, COFs have a wide range of applications that include gas separation, capture and storage, heterogeneous catalysis,^[3–5] energy storage and production, chemo-sensing, organic semiconductors, and many others.

Here we combine DFT calculations and Grand-Canonical Monte Carlo (GCMC) calculations based on classical force field to explore the interplay between the pore size and pore functionalization on the capture of gases such as CO₂, CH₄ and H₂ by two-dimensional covalent organic frameworks.

Methodology

The set of initial structures were generated using our in-house software to generate organic lattice structures. For 2D COFs, structures were generated with the network topologies hcb and hcb-a. All 2D structures were simulated with AA stacking considering two sheets per unit cell.

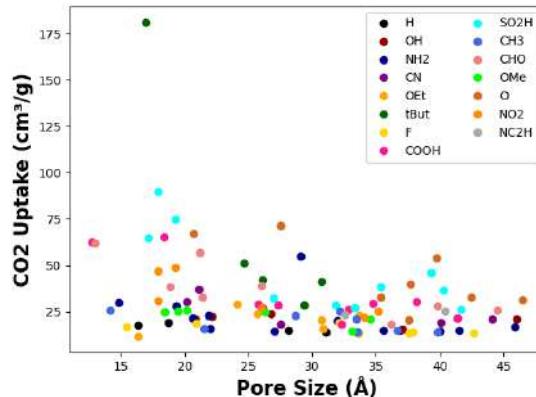
DFT calculations under periodic boundary conditions were performed using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional with DFT-D3(BJ) dispersion corrections. The Quickstep code of the CP2K v 8.2 package was used, employing GTH pseudopotentials, DZVP-MOLOPT-SR contracted Gaussian basis sets, and an auxiliary plane wave basis set.

Density-derived electrostatic charges are calculated within the DDEC6 method as implemented in the Chargemol software. The charges were derived based on the electron density of the optimized structures computed from CP2K.

Force field-based Grand-Canonical Monte Carlo (GCMC) simulations were performed using the RASPA2 package. For all GCMC simulations, 2000 initiation cycles and 10000 running cycles. A Lennard-Jones potential with parameters taken from the TraPPE force field was used to treat the van der Waals interactions of adsorbed molecules and DREIDING for the framework atoms.

Results

Our results show that for the three gases tested the total volume of gas captured depends much more directly on the type of pore functionalization than on the pore size. Functional groups such as tBut, OH, COOH, OMe, SO₂H and OEt systematically capture the volume of gas captured, particularly for structures with pores below 25 angstroms.



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Computational Study of Pt(IV) Complexes with Antitumoral Potential: Assessment of Standard Reduction Potential

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Keywords: Pt(IV) Complexes, Reduction Potential, Solvent Effects.

Introduction

In 1965 the antitumor properties of cisplatin were discovered and since then it has been one of the most used antineoplastics in cancer chemotherapy. Despite its success, its high toxicity and side effects attributed to its low specificity, generate the need to search for new drugs. In this context, Pt(IV) complexes have been presented as an alternative to Pt(II) complexes for cancer chemotherapy, due to their great inertia and stability, and can be administered orally.¹ Understanding the Pt(IV) → Pt(II) reduction mechanism and its activation stage in the intracellular environment is of fundamental importance in the search for new antitumor compounds. Thus, the present work aims the construction of a computational protocol, evaluating the role of theory level, basis set and solvent effects in predicting the reduction potential of Pt(IV) complexes.

Methodology

For the construction of the computational protocol for the prediction of reduction potential (ϵ^0) of Pt(IV) complexes, a set of 8 Pt (IV) complexes was selected, presenting experimental data for the reduction potential, measured by cyclic voltammograms in dimethylformamide (DMF) as solvent, with reference to the Ag/AgCl electrode, where the potential data of reduction range from -850 mV to -630 mV.² The analyzes were performed using ΔG values obtained from the construction of a thermodynamic cycle using the optimized structures and gas phase calculated frequencies. For the inclusion of solvent effects, continuous solvation models IEF-PCM(UFF), SMD and C-PCM were considered. DFT calculations were performed with the hybrid functional B3LYP, and 64 protocols were constructed from distinct combinations of basis set (metal/ligands) and the calculated values were obtained through eq. (1). All calculations were performed using the Gaussian 09 Rev. D.01 program.

$$\epsilon^0 (\text{Pt}^{4+} \rightarrow \text{Pt}^{2+}) = \left[-\frac{\Delta G^\circ_{\text{Pt,sol}}}{2} - \epsilon^0_{(\text{SHE}),\text{aq}} \right] \quad (1)$$

Results

The results suggest that the IEF-PCM(UFF) and C-PCM solvation models are the most suitable for the

description of solvent effects, compared to the SMD model. The mDZP basis set that stood out was previously proposed in the extensive study conducted by Paschoal *et al.*, on the importance of the level of theory and the basis set for theoretical predictions of the structure and reactivity of cisplatin.³ Thus, the P52 protocol (B3LYP/mDZP/6-31+G-2df) was the one with the lower mean absolute deviations (DAM) for both models, 29 and 28 mV, respectively (Table 1).

Table 1. Data for ϵ^0 , relative deviation (MRD) and mean absolute deviation (MAD) (mV).

P52 - B3LYP/mDZP/6-31+G-2df							
	IEF-PCM			C-PCM			Exp.
	Calc.	MRD	MAD	Calc.	MRD	MAD	
1	-887	4	37	-880	3	30	-850
2	-871	2	21	-864	2	14	-850
3	-872	6	52	-865	5	45	-820
4	-667	9	63	-661	9	69	-730
5	-683	4	27	-677	5	33	-710
6	-696	3	24	-690	4	30	-720
7	-658	0	2	-652	1	8	-660
8	-634	1	4	-630	0	0	-630
		4	29		4	28	

Conclusion

In the present study, an analysis was performed to find a suitable computational protocol for predicting the reduction potential of Pt(IV) complexes. So far, the best protocol (B3LYP/mDZP/6-31+G-2df) obtained a DAM of only 28 and 29 mV, for the IEF-PCM(UFF) and C-PCM solvation models, respectively, an excellent alternative for computational prediction of the reduction potential of Pt(IV) complexes.

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Elementary catastrophes in photochemically activated reactions: The singlet Paterno-Büchi reaction.

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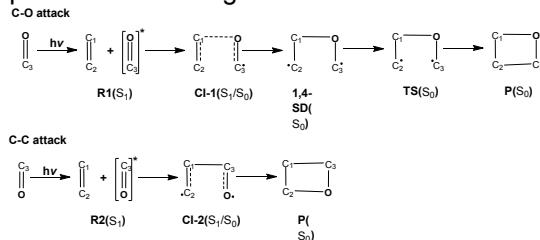
Keywords: Paterno-Büchi, BET, Pairing density.

Abstract

The photochemically activated Paterno-Büchi reaction mechanism following the singlet excited-state reaction path was analyzed based on a bonding evolution framework. The electronic rearrangements, which describe the mechanism of oxetane formation via carbon-oxygen attack (C-O), comprise the electronic activation of formaldehyde accumulating of pairing density on the O once the reaction system is approaching the conical intersection point.

Introduction

One of the most successful interpretations of reaction mechanics lies in the real-space, where real-space functions such as the electron density, and the density matrix derivatives quantities along any reaction coordinate. The bonding evolution theory (BET)[1] constitutes an interesting model which allows associates abrupt changes in the electron localization function (ELF)[2] topology to each elementary bonding stage i.e breaking/forming bonds. These abrupt changes are known as catastrophes Within the theoretical background of Thom's catastrophe theory. BET has provided information about electron pair rearrangements occurring in a broad of chemical reactions that take place in the ground state. The application of the BET model in the excited-state reactions is an unexplored field of research. In this work, we analyzed the photochemical singlet Paterno-Büchi reaction:



Methodology

For both C-C and C-O mechanisms were calculated minimum energy paths connecting the reactants in the S_1 excited state, the minimum conical intersection point, and intermediates and products in the ground state. The reaction paths were computed at CASSCF (6, 5)/6-31g level in the S_1 and S_0 states. The ELF calculation was carried out within the natural orbital formulation proposed by Mattito *et al.* [3], [4]. The characterization of elementary catastrophes was performed via Hessian matrix calculation.

Results

The main results of this work can be summarized in the following scheme: This information about the Paterno-Büchi mechanism was obtained from ELF topology and catastrophe characterization, for example: The activation of formaldehyde reactants occurs in the excited state. Locally, this process occurs due to the concentration of pairing density near both C and O atoms. The first C-O bond is formed in the ground state surface via pairing density migration flowing from O surroundings to the C neighborhood. The ring closure via C-C bond-forming occurs in the ground state surface in the proximity of the transition state (TS). Such an electronic rearrangement takes place via pair density migration from the C3 atom towards C2 one.

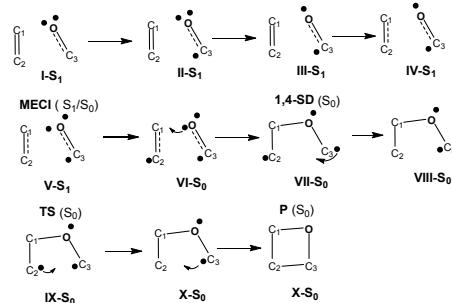


Figure 1. Electronic pair rearrangements occurring in the Paterno-Büchi reaction.

Conclusions

(i) The elementary catastrophes exist in the excited state surface, and these can be characterized via hessian matrix calculations. (ii) The fold-type catastrophes are the topological fingerprints for C-C bond formation occurring in the Paterno-Büchi reaction. (iii) The S_1 excited state surface constitutes a preparatory stage in the Paterno-Büchi, wherein the C and O atoms (in formaldehyde) are accumulating pairing density.

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Do Double Hybrids Provide Accurate Chemical Shifts? A Benchmark Assessment of Density Functional Theory for Proton NMR

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Keywords: density functional methods, proton NMR, structure elucidation, natural products.

INTRODUCTION

NMR spectroscopy has become an invaluable characterization technique routinely applied across the molecular sciences. Quantum chemical calculations of NMR parameters such as chemical shifts enabled by affordable DFT methods have developed into an ancillary tool in the structure elucidation of complex molecules and even reassignments.¹

We evaluated a series of DFT methods with a focus on double-hybrid density functionals (DHDFs) as they represent the highest rank or rung 5 of Jacob's ladder and, therefore, recommended for their superior accuracy. Surveys of NMR parameters using DHDFs remains scarce in the literature.^{2,3} We aimed at addressing the central question of whether current DHDFs perform better than lower-rung DFT methods in predicting ¹H NMR chemical shifts.⁴

COMPUTATIONAL METHODS

Chemical shifts were computed on M06-2X/6-311+G(2d,p) optimized geometries using cc-pVXZ (X=T,Q) and pcSseg-*n* (*n*=0-4) basis sets. For all DHDFs, the resolution of identity scheme RIJK was applied with matching auxiliary basis sets (e.g., cc-pVTZ with cc-pVTQ/JK and cc-pwCVQZ/C). The gauge-independent atomic orbital (GIAO) method was used to compute isotropic magnetic shielding constants. Proton shifts $\delta(^1\text{H})$ were determined relative to TMS calculated at the same level of theory. Solvent effects were computed within the conductor-like polarizable continuum model (CPCM). Calculations were performed using Gaussian 09 (D.01) and ORCA 4.2.1 codes.

RESULTS

To benchmark the performance of density functionals (DFs), two ¹H NMR data sets were constructed: NMRH33 with 33 individual proton shifts spanning over 8.42 (0.22 to 8.62) ppm and NMRH148 (range: 9.72 ppm).

In general, the cc-pVTZ basis set yielded smaller mean absolute deviations (MADs) than pcSseg-2. Results for all DFs evaluated using cc-pVTZ are shown in Fig. 1. The popular hybrid-GGA B3LYP functional performed reasonably well (MAD 0.16 ppm; max 0.42 ppm) with results comparable to the

best performing DHDF (revDSD-BLYP: MAD 0.16; max 0.35 ppm). The latter yields a smaller maximum deviation, but at a substantially higher computational cost. TPSS family exhibited some of the best overall performance except for LC-TPSS (MAD 0.30 ppm). The excellent performance of the revTPSS functional (MAD 0.10, max 0.26 ppm) is a notable outcome, which has been overlooked in previous studies.

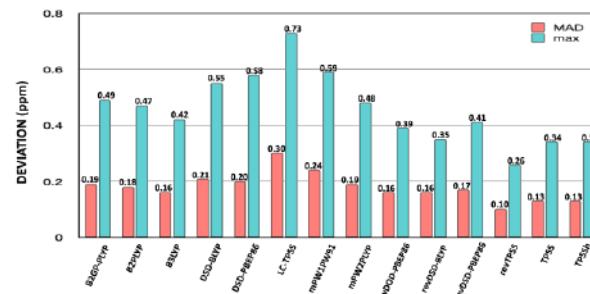


Figure 1. Results for NMRH33 data set: mean absolute deviation (MAD) and maximum deviation (max) in ppm for all tested density functional with the cc-pVTZ basis sets.

Results presented are supported by the evaluation of relevant variables that may implicate in error compensation including basis set convergence and geometry effects. A set of natural products were also considered for providing real-world, challenging cases for ¹H NMR shift prediction.

CONCLUSIONS

Despite overall recommendations of currently available DHDFs for various properties, our results indicate that the case of ¹H NMR chemical shifts is an important exception. DHDFs offered no benefit over hybrid- and meta-GGA density functionals.

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ESTUDO COMPUTACIONAL DE INTERAÇÕES SIMULTÂNEAS DE HALOGÊNIO ANFOTÉRICO EM COMPLEXOS COM ÁTOMOS DE CARBONO E OXIGÊNIO

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Palavras-Chave: *Interações, Propriedades de recobrimento, Propriedades QTAIM.*

INTRODUÇÃO

Nos últimos anos, as emissões de dióxido de carbono (CO_2) na atmosfera aumentaram devido a queima de combustíveis fósseis. Além disso, muitas indústrias liberam gases de efeito estufa que são responsáveis pelas mudanças climáticas do planeta [1]. Dessa forma, a redução das emissões de CO_2 na atmosfera é crucial para melhorar o clima, mas esse processo de redução é considerado um longo [3]. Os combustíveis fósseis possuem um papel imprescindível na geração de energia [5]. Sendo assim, a captura de CO_2 tornou-se uma questão essencial que precisa ser resolvida. Diante do exposto, a literatura tem reportado que os líquidos iônicos (LIs) apresentam um potencial para captura de CO_2 , estimulando muitos pesquisadores a explorar várias estruturas moleculares [2]. Bhargava e Balasubramanian investigaram a interação detalhada de uma molécula de CO_2 com diferentes ânions usados em LIs baseados na teoria do funcional da densidade [4]. No presente trabalho, relatamos a comparação de nosso modelo de recobrimento de ligações químicas (OP) [3] com o modelo da Teoria Quântica de Átomos em Moléculas (QTAIM). Nessa perspectiva, os sistemas estudados foram $\text{CO}_2\cdots\text{X}$, onde $\text{X} = \text{CO}_2$, BrF , ClBr , BrCl e BrBr .

METODOLOGIA

As geometrias dos sistemas estudados foram otimizadas no nível ω B97X-D com o conjunto de funções de base aug-cc-pVDZ usando o programa GAMESS. Os orbitais moleculares localizados necessários ao modelo OP foram obtidos usando o método Pipek-Mezey. As propriedades de recobrimento (repulsão de Coulomb $J_{\text{OP}}^{\text{intra}}$ e densidade ρ_{OP}) foram calculadas usando nosso software ChemBOS. A análise QTAIM foi realizada usando o software Multiwfn para calcular as propriedades dos pontos críticos da ligação (densidades de elétrons ρ_{BCP} , e Laplaciano $\nabla^2\rho_{\text{BCP}}$ de densidade no BCP).

RESULTADOS

A DFT foi usada para realizar cálculos de geometria de equilíbrio, cálculo de função de onda, localização de orbitais moleculares, análise de propriedades de recobrimento e análise topológica dos 5 sistemas moleculares estudados neste trabalho. Na Tabela 1 é possível observar os resultados dessas propriedades de ligações químicas para essas interações, obtidas através dos

modelos OP e do modelo QTAIM. Os valores de $\nabla^2\rho_{\text{BCP}}$ para as interações $\text{CO}_2\cdots\text{X}$ são positivos, mas baixos para a maioria dos sistemas, indicando pouca ou nenhuma concentração de carga na região da ligação química. Além disso, exibem um comportamento de interação fraca, em comparação com os outros sistemas estudados, tanto para os resultados de QTAIM quanto o modelo OP.

Table 1. Calculated chemical bonding properties: Bond distance R (in Å), Intra-overlap repulsion $J_{\text{OP}}^{\text{intra}}$ (E_h), and density ρ_{OP} (e), electron density ρ_{BCP} (e/a_0^3) and Laplacian $\nabla^2\rho_{\text{BCP}}$ (e/a_0^5) of density at the BCP.

System	R	$J_{\text{OP}}^{\text{intra}}$	ρ_{OP}	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$
1 $\text{CO}_2\cdots\text{CO}_2$	3.25	1.65	-0.33	0.45	0.59
2 $\text{CO}_2\cdots\text{BrF}$	2.81	0.31	-0.15	0.01	0.06
3 $\text{CO}_2\cdots\text{ClBr}$	3.62	0.25	-0.14	0.01	0.02
4 $\text{CO}_2\cdots\text{BrCl}$	3.00	0.37	-0.17	0.01	0.04
5 $\text{CO}_2\cdots\text{BrBr}$	3.09	0.22	-0.13	0.01	0.03

Na Figura 1, nota-se os mapas de densidade dos orbitais localizados utilizados na análise de recobrimento.

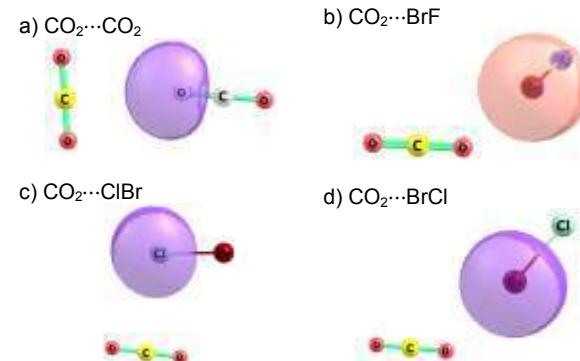


Figura 1. Orbitais moleculares localizados das interações nos sistemas estudados – isovalor $0.06\text{ }e/a_0^3$.

CONCLUSÃO

Mais análises estão sendo feitas, incluindo a avaliação detalhada do modelo recobrimento utilizando funcionais mais modernos com correção de dispersão.

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COMPUTATIONAL STUDY OF REDUCTION POTENTIAL OF Ru(III)/Ru(II) COMPLEXES

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Keywords: Reduction potential, Ru complexes, DFT.

Introduction

Since the discovery of the anticancer potential of ruthenium-based complexes, several candidates have been reported as promising for the treatment of cancer. The development of metal-based antitumor drugs originated with the discovery of antitumoral properties of cisplatin, however, its serious side effects represent a limitation for its clinical use. Ruthenium (Ru) complexes with different ligands have been successfully studied as promising antitumor drugs. Ruthenium-based anticancer drugs are among the most explored and advanced next-generation metallotherapeutics, such as NAMI-A and KP1019, two ruthenium complexes undergoing clinical trials. Thus, the present study presents the construction of a computational protocol for the prediction of the reduction potential of Ru(III) complexes with antineoplastic potential.

Methodology

The $[Ru(H_2O)_6]^{3+}/[Ru(H_2O)_6]^{2+}$ redox process, that present experimental data available in the literature, was selected for the build of computational protocol for the prediction of reduction potential (ε^0). The reduction potential was obtained according to eq. (01) using the ΔG values obtained from the construction of a thermodynamic cycle, with the optimized structures and thermal corrections obtained in gas phase. For the inclusion of solvent effects, the implicit C-PCM model was used, with the dielectric constant set for water. DFT calculations were performed using 21 distinct functionals with the def2-SVP basis sets (metal/ligands). All calculations were performed using the ORCA 5.0.1 program.

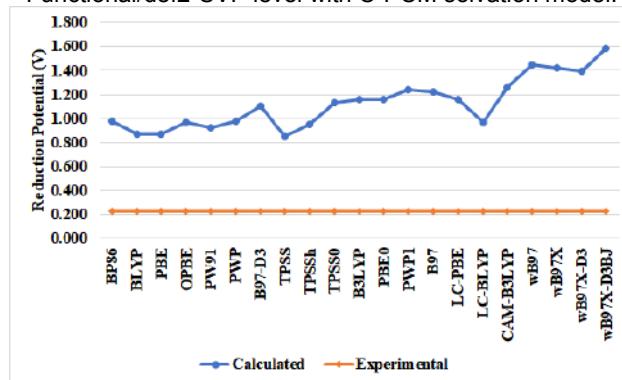
$$\varepsilon^0(V) = 27.2114 \times (G_{ox} - G_{red}) - \varepsilon_{abs}^0(SHE) \quad (01)$$

Results and Discussion

From the calculated results (Fig. 1), it can be seen how the reduction potential is sensitive to the DFT functional used. Although the calculated values are far from the experimental value, a variation of 725 mV was observed only with the change in the density functional. The calculated results indicate that the

functional TPSS (0.856 V) and PBE (0.868 V) are the most suitable for the description of the reduction potential. In the next steps of the work, the effect of Ru and ligands basis sets, the continuous solvation model used and the relativistic effects will also be evaluated in order to find the appropriate computational protocol for the study of the reduction potential of ruthenium complexes.

Fig. 1. Calculated reduction potential (ε^0 , V) for $[Ru(H_2O)_6]^{3+}/[Ru(H_2O)_6]^{2+}$ redox process at DFT-Functional/def2-SVP level with C-PCM solvation model.



Conclusions

The study presented an analysis of the role of the DFT functional in predicting the reduction potential of ruthenium complexes. The results indicate that the functional TPSS and PBE are the most indicated. Other analyzes will still be carried out in later stages of the work.

Acknowledgments

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STRUCTURE-ANTIOXIDANT ACTIVITY RELATIONSHIPS OF PYRAZOLE DERIVATIVES

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keywords: DFT, PCA, Pyrazole

INTRODUCTION

Pyrazoles are potent medicinal scaffolds and exhibit a full spectrum of biological activities¹. A quantum chemical and chemometric study of nine 9 pyrazole analogs was also applied to the compounds to establish the relationship between molecular structure and antioxidant activities.

METHODS

The DPPH radical scavenging model is extensively used to evaluate antioxidant activities and was performed at various concentrations of compounds (1-9) according to the literature protocol, with some modifications. The lowest-energy conformation of each molecule was further optimized with the Gaussian G09 software package². All calculations were carried out using the exchange correlation functional³ M062X and the basis set 6-311++G(d,p). By applying PCA (Principal Component Analysis) procedure^{4,5} to the selected descriptors by Fisher's weight, after many attempts, the best result was obtained with three molecular descriptors: bond angle A1 between atoms 17, 16 and 28, bond angle A2 between atoms 15, 16 and 28 and bond order OL between atoms 9 and 36.

RESULTS AND DISCUSSIONS

In Figure 1, the atomic numbering is shown for the pyrazole derivatives and the table presents atom numbering for the substituents

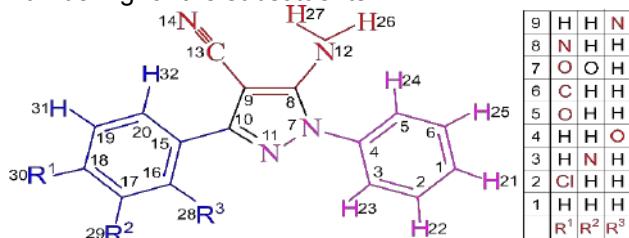


Figure 1. Atomic numbering for pyrazole derivatives used throughout the calculation.

Figure 2a shows that the active compounds have negative scores, and the active compounds are on the left-hand side, while the inactive compounds are on the right-hand side. Indeed, we can draw a vertical line that separates the two groups. Figure 2a also shows that PC1 alone is responsible for the discrimination; it accounts for about 64.75% of the total variance in the data. PC1 and PC2 together account for 92.50% of the variance.

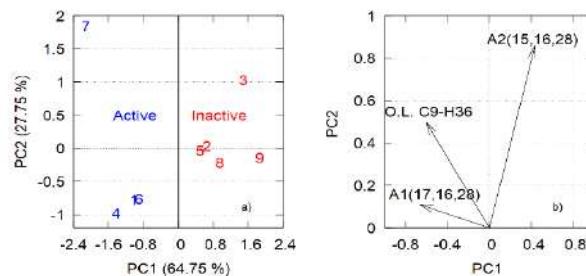


Figure 2. Graphical representations of the scores and loadings for PC1 and PC2.

We know all selected descriptors have positive values, and Figure 2a shows that the active compounds have negative scores. According to Figure 2b and Equation 1 for PC1, which is responsible for the classification, for a compound to be classified in the active class, it should have higher values for the descriptors bond angle A1 and bond order OL C9-H36, and a lower value for bond angle A2.

$$PC1 = -0.67A1 - 0.60OL + 0.43A2 \quad (1)$$

CONCLUSIONS

The PCA of the molecular descriptors of pyrazole-based compounds, as calculated at the M062X/6-311++G(d,p) level of theory, showed that three descriptors: bond angles A1 and A2 and bond order OL can be used to categorize these compounds into two classes.

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Ab initio multiconfigurational calculations on electron trap depths in Pr,M-codoped lutetium oxide doped (M=Ti, Zr and Hf)

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Long-term energy storage and thermoluminescence in phosphors based on cubic Lu₂O₃:Pr are achievable via introduction of d metal co-dopants. It was assumed from the vast experimental data that by photoionization of Pr³⁺ to Pr⁴⁺ occurs, and that d orbitals of the co-dopants contain (trap) the electrons formed upon excitation.

The experiments indicate two mechanisms of the electron release: an excitation to conduction band with the following recombination at Pr site, or a tunneling mechanism which does not involve conduction band. Given the fact that Lu states were not considered (i.e. no conduction band model was provided) – the results should be viewed as the tunneling trap depth. However, they might also be relevant to the mechanism with the band.

We have used RASSCF / CASPT2 / RASSI-SO (PrO₆⁹⁻ cluster, Pr³⁺; PrO₆⁸⁻ cluster, Pr⁴⁺; MO₆⁹⁻ clusters, M³⁺, M=Ti, Zr, Hf) and CCSD (MO₆⁸⁻ clusters, M⁴⁺) in order to obtain the total energies of the mentioned clusters of metal cations and their surrounding oxygens. The clusters were embedded in the c-Lu₂O₃ lattice by Ab Initio Model Potential (AIMP) and a sphere of point charges. For each cluster, total electronic energies were calculated for a series of geometries corresponding to a path along a certain vibrational normal mode. The total energy of the state with the trapped electron was represented by a sum of the energies of PrO₆⁸⁻ and MO₆⁹⁻ clusters (a Pr⁴⁺, M³⁺ system). The total energy of the state without the trapped electron was represented by a sum of the energies of PrO₆⁹⁻ and MO₆⁸⁻ clusters (a Pr³⁺, M⁴⁺ system).