



## Theoretical investigation of nitric oxide interaction with aluminum phthalocyanine

Valter H.C. Silva<sup>a,\*</sup>, Marcos P. Martins<sup>a</sup>, Heibbe C.B. de Oliveira<sup>b</sup>, Ademir J. Camargo<sup>a</sup>

<sup>a</sup> Unidade Universitária de Ciências Exatas e Tecnológicas, Universidade Estadual de Goiás, P.O. Box 459, 75001-970 Anápolis, GO, Brazil

<sup>b</sup> Instituto de Química, Universidade de Brasília, 70919-970 Brasília, DF, Brazil

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### ABSTRACT

Nitric oxide (NO) is an extremely toxic compound formed during combustion, predominantly at high temperatures, and it is among the most important atmospheric pollutants. However, this compound has interesting biological activities, since it can control important biological processes in living organisms. With the aim of developing new materials that can be used as selective chemical sensors or as biomedical NO delivery agents we carried out a quantum mechanical study of the interaction of NO with aluminum phthalocyanine (AlPc) at B3LYP/6-31G\* level. The calculation results show clearly that the complexation of NO with AlPc depends on the latter's oxidation state. NO is more strongly bonded to AlPc in the reduced state (−33.77 kcal/mol) than in the oxidized state (−4.96 kcal/mol). By applying the Fukui function and analysis of the Frontier molecular orbital, it was possible to explain the situation within which nitric oxide interacts with AlPc.

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### 1. Introduction

Nitrogen oxides, NO<sub>x</sub>, is a generic term used to refer to the class of oxides of nitrogen, and nitric oxide (NO) is the main representative of this class. Nitric oxide is a diatomic radical, a colorless, flammable gas with a slight odor that has proved to be very active in certain biological processes: it regulates blood pressure, acts as a neurotransmitter and helps the immune system's ability to kill intracellular parasites [1–4]. Considering these interesting properties of nitric oxide, we decided to model new material that can be used as a selective chemical sensor for NO and/or as an NO carrier in a biological system [5,6]. Our attention was focused on aluminum phthalocyanine (AlPc), an aromatic compound with 18 $\pi$  electrons that can be easily synthesized, and which has high thermal and chemical stability and low biological toxicity. These features make phthalocyanine the target of intense theoretical and experimental studies to develop new materials and drugs [7–12]. Among their applications, we can mention the use of phthalocyanine in the construction of chemical sensors [7,13,14], semiconductor materials [7,14,15], photoconductors [7,16–18], electrochromic display [7,19,20], optical recording materials [21,22], catalytic properties for organic reactions [23–27] and potential applications in the treatment of many kinds of diseases like infections and visual and neural degenerative diseases [7,28–31].

Aluminum metal is an interesting choice for the phthalocyanine complex due to its small size and high charge density, which make strong electrostatic interactions possible and, in turn, a variation in the charge density of the ligands attached to them [23,32–34]. Furthermore, the oxidation properties of aluminum and aluminum phthalocyanines are not yet fully understood [35–37]. Therefore, the aim of the present work was to study theoretically the nature of the interaction between nitrogen oxides and AlPc in different oxidation states (0, +1), observing if AlPc can be employed as a selective chemical sensor for NO and as an NO carrier in biological systems. Different oxidation states can influence the interaction between molecules [38,39], and another focus is to evaluate this change in AlPc when interacting with NO.

The nature of the interactions between chemical reagents is better understood by carrying out calculations on the interaction energies and by global and local descriptors of electronic structure, such as chemical *hardness* ( $\eta$ ), *softness* ( $S$ ), and *Fukui functions* ( $f$ ). These parameters have provided useful information about thermodynamic aspects of chemical reactions and reactivity sites [40–43]. The Hard–Soft Acid–Base (HSAB) principle utilizes the parameters *hardness* and *softness* to state that “*hard acids* prefer to coordinate to *hard bases*, and *soft acids* to *soft bases*” [40,44]. The *Fukui function* is a local parameter responsible for identifying privileged sites of reactivity in the molecules, and it states that the highest *Fukui function* value in the molecule is the preferred site for the reaction to take place.

This paper is organized as follows: in Section 2 we present the computational details performed in this work. Analysis and

\* Corresponding author. Tel.: +55 62 33281162; fax: +55 62 33281155.  
E-mail address: [fatiolleg@ueg.br](mailto:fatiolleg@ueg.br) (V.H.C. Silva).

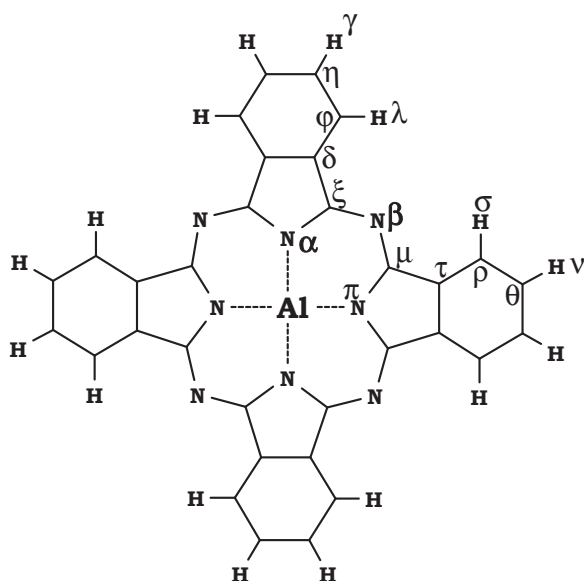


Fig. 1. Nomenclature for aluminum phthalocyanine (AlPc).

discussions of results are presented in Section 3. In Section 4, we display our final conclusions.

## 2. Computational details

The geometry and nomenclature used in the calculations for AlPc are shown in Fig. 1. The calculations reported in this paper were carried out using the Kohn–Sham density functional theory (DFT) with Beck three-parameters hybrid exchange–correlation functional, known as B3LYP [45–47], and the split-valence basis set 6-31G\*, implemented in the Gaussian 03 program suite [48]. The local minima on the potential energy hypersurface were characterized by the computation of the vibrational frequencies at the same level used in the geometry optimizations. The absence of vibrational modes with imaginary frequencies showed that the optimized molecular geometry was found at a local minimum point on the potential energy hypersurface. Since the binding energies include a basis set superposition error (BSSE) [49,50], due to the supermolecule approach, the full counterpoise method of Boys and

Bernardi [51] was employed to estimate the BSSE, resulting in the corrected binding energy ( $\Delta E$ ) values. All the bond order indices were obtained from natural population analysis (NPA) using the NBO 3.1 [52] program implemented in the Gaussian 03 program package. The atomic partial charges on the atoms were obtained from the Mulliken scheme at B3LYP/6-31G\* level.

Since zero-point vibrational energy (ZPVE) contributions have a non-negligible effect on the stabilities of NO bonded complexes, we evaluated these contributions using the B3LYP/6-31G\* level of theory. The corrected binding energies for the complexes were calculated as follows [53]

$$\Delta E = \{E[(\text{NO})\text{AlPc}] + E[(\text{NO})\text{AlPc}]_{\text{ZPVE}} - \{E[\text{AlPc}]_{\text{BSSE}} + E[\text{AlPc}]_{\text{ZPVE}} + E[\text{NO}]_{\text{BSSE}} + E[\text{NO}]_{\text{ZPVE}}\}, \quad (1)$$

where  $\Delta E$  represents the interaction energy and  $E$  is the calculated energy at B3LYP/6-31G\* level for each species. The hardness ( $\eta$ ) and softness ( $S$ ) were obtained using the functions  $\eta = E_{(N_0-1)} - 2E_{(N_0)} + E_{(N_0+1)}$  and  $S = 1/\eta$ , where  $E$  stands for ground-state energy and  $N_0$  is the number of electrons in the system's ground state. The Fukui functions ( $f$ ) were calculated according to equations  $f_x^+ \approx \rho_x^{\text{HOMO}} = \sum_i |c_i|_{\text{HOMO}}^2$ ,  $f_x^- \approx \rho_x^{\text{LUMO}} = \sum_i |c_i|_{\text{LUMO}}^2$ , and  $f_x^0 \approx (f_x^+ + f_x^-)/2$ , which were implemented in the MOCALC program. [54,55]. These equations govern the nucleophilic, electrophilic, and radical attack, respectively. In the Fukui function above,  $x$  stands for atom specification and  $c_i$ 's are the coefficients for atom  $x$  in the Frontier molecular orbital.

## 3. Results and discussion

### 3.1. $[\text{AlPc}]^+$ and $[\text{AlPc}]^0$ complexes

The first step in this study was to do a full optimization of AlPc in gas phase, in both oxidation states (oxidized state  $[\text{AlPc}]^+$  and reduced state  $[\text{AlPc}]^0$ ) using the B3LYP/6-31G\* level. The calculation results are shown in Fig. 2 and in Table 1. The data analyses show that AlPc in its oxidized state in gas phase has a planar geometric structure, with symmetry belonging to the point group  $D_{4h}$ . In its reduced state, i.e., when the charge on the system is zero, there is significant change in the geometry structure, as can be seen in Fig. 2. The main change is the projection of the Al atom from the molecular plane by about 0.56 Å. This calculated value is 0.16 Å greater than the X-ray value [56] for chloro(phthalocyaninato)aluminum(III) ( $\text{AlPcCl}$ ). The presence of

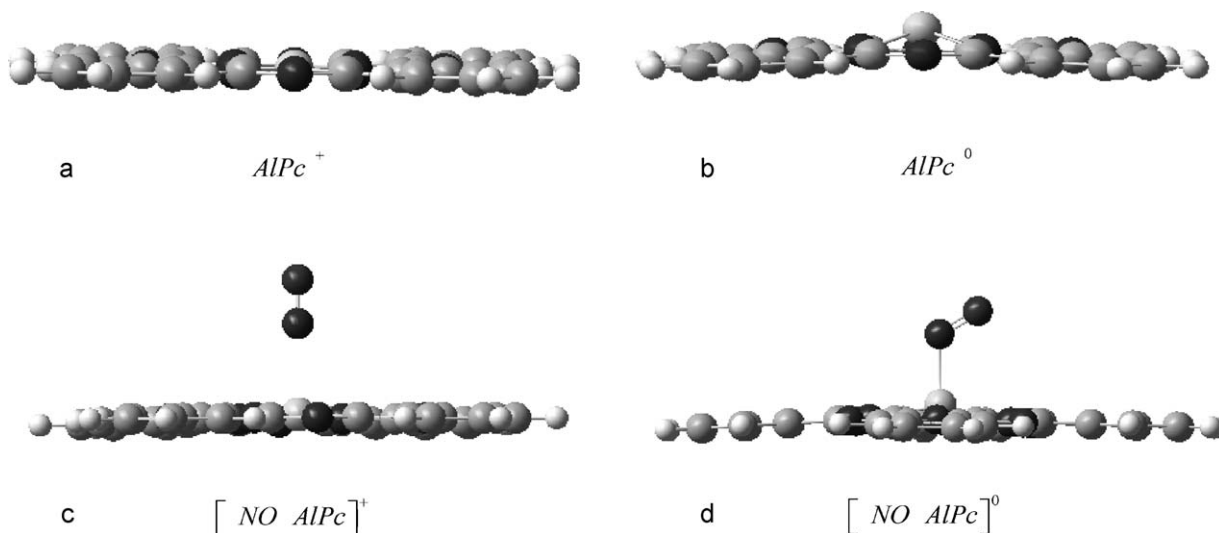


Fig. 2. Optimized structures using the B3LYP/6-31G\* level for AlPc and (NO)AlPc in the reduced and oxidized states.

**Table 1**

Theoretical bond length (in Å) and angle (in°) for AlPc and (NO)AlPc in the reduced and oxidized states at B3LYP/6-31G\* level and experimental parameters for AlPc in the reduced state.

	[AlPc] <sup>+1</sup>	[AlPc] <sup>0</sup>	X-ray <sup>a</sup>	[(NO)AlPc] <sup>+1</sup>	[(NO)AlPc] <sup>0</sup>
ON–Al	–	–	–	2.327	1.957
Al–Plane	0.000	0.559	0.399	0.103	0.394
Al–N <sup>α</sup>	1.922	2.020	1.956	1.928	1.971
N <sup>α</sup> –C <sup>ξ</sup>	1.398	1.380	1.465	1.396	1.383
C <sup>ξ</sup> –N <sup>β</sup>	1.318	1.324	1.334	1.319	1.322
C <sup>ξ</sup> –C <sup>δ</sup>	1.444	1.454	1.358	1.445	1.453
C <sup>δ</sup> –C <sup>ψ</sup>	1.398	1.396	1.458	1.398	1.396
C <sup>ψ</sup> –C <sup>η</sup>	1.392	1.393	1.547	1.392	1.392
C <sup>η</sup> –H <sup>γ</sup>	1.086	1.086	–	1.086	1.086
C <sup>ψ</sup> –H <sup>λ</sup>	1.085	1.085	–	1.085	1.085
Al–N <sup>α</sup> –C <sup>ξ</sup>	126.68	125.33	128.90	126.44	125.34
Al–N–O	–	–	–	179.82	120.42
N <sup>α</sup> –C <sup>ξ</sup> –N <sup>β</sup>	126.96	127.55	120.05	127.07	127.45
C <sup>ξ</sup> –N <sup>β</sup> –C <sup>μ</sup>	122.72	122.50	132.13	122.78	122.66
C <sup>ξ</sup> –C <sup>δ</sup> –C <sup>ψ</sup>	131.82	132.33	126.58	131.86	132.24
C <sup>δ</sup> –C <sup>ψ</sup> –C <sup>η</sup>	117.29	117.53	110.97	117.30	117.51

<sup>a</sup> X-ray values for [(Cl)AlPc]<sup>0</sup> from Ref. [56].

the chloride ion and the intermolecular interactions in the solid state decrease the out-of-plane projection of the Al atom. Furthermore, the observed disorder in (AlPc)Cl crystal structure refined by Wynne [56] gave high values for overall refinement indices. The average absolute deviations of the calculated values to oxidized and reduced states, with experimental results for the bond length, are about 0.12 and 0.09 Å, respectively (see Table 1). The calculated data also show an increase of 0.1 Å in the Al–N<sup>α</sup> bond length in the reduced state, suggesting that this bonding is weaker than in the oxidized state. Except for a slight decrease of 1.4° in the angle Al...N<sup>α</sup>–C<sup>ξ</sup>, the other geometric parameters are not significantly changed with the reduction of the oxidized complex [AlPc]<sup>+</sup> (see Table 1).

The bond orders for the AlPc complexes are shown in Table 2. The calculated bond orders for the Al–N<sup>α</sup> bond are 0.40 in the oxidized state and 0.29 in the reduced state, which represent a decrease of 27.5% in the bond order when the complex is reduced. The calculated partial atomic charges using the Mulliken procedure can be seen in Table 3. It is observed that the aluminum atom presents a positive charge, with values ranging from 0.58 ([AlPc]<sup>0</sup>) to 0.98 ([AlPc]<sup>+</sup>). The values of the charge in the aluminum to reduced and oxidized states show that a considerable part of the charge acquired by the AlPc complex, when it is reduced, remains close to the Al atom.

The Frontier molecular orbitals are important descriptors to understand chemical interactions, clarifying key features in the chemistry of complexes and solids like reactivity and stability. The Highest Occupied Molecular Orbital (HOMO) is directly related to the ionization potential and chemical reactivity in electrophilic reactions, while the Lowest Unoccupied Molecular Orbital (LUMO) is related to the electronic affinity and susceptibility to nucleophilic

**Table 2**

Bond order for AlPc and (NO)AlPc in the reduced and oxidized states at B3LYP/6-31G\*\*/NBO 3.1 level.

	[AlPc] <sup>+1</sup>	[AlPc] <sup>0</sup>	[(NO)AlPc] <sup>+</sup>	[(NO)AlPc] <sup>0</sup>
N–Al	–	–	0.22	0.49
N–O	–	–	2.13	1.96
Al–N <sup>α</sup>	0.40	0.29	0.37	0.32
N <sup>α</sup> –C <sup>ξ</sup>	1.14	1.20	1.15	1.19
C <sup>ξ</sup> –N <sup>β</sup>	1.39	1.37	1.39	1.36
C <sup>ξ</sup> –C <sup>δ</sup>	1.12	1.10	1.12	1.11
C <sup>δ</sup> –C <sup>ψ</sup>	1.33	1.35	1.33	1.34
C <sup>ψ</sup> –C <sup>η</sup>	1.48	1.47	1.48	1.48
C <sup>η</sup> –H <sup>γ</sup>	0.91	0.91	0.91	0.91
C <sup>ψ</sup> –H <sup>λ</sup>	0.90	0.91	0.90	0.91

**Table 3**

Partial atomic charges (in e units)<sup>a</sup> obtained from Mulliken population analysis for AlPc and (NO)AlPc in the reduced and oxidized states at B3LYP/6-31G\* level.

	[AlPc] <sup>+1</sup>	[AlPc] <sup>0</sup>	[(NO)AlPc] <sup>+</sup>	[(NO)AlPc] <sup>0</sup>
N	–	–	0.17	–0.08
O	–	–	–0.09	–0.24
Al	0.94	0.58	0.97	0.89
N <sup>α</sup>	–0.67	–0.66	–0.67	–0.66
C <sup>ξ</sup>	0.49	0.49	0.48	0.49
N <sup>β</sup>	–0.53	–0.56	–0.53	–0.55
C <sup>δ</sup>	0.08	0.08	0.08	0.07
C <sup>ψ</sup>	–0.17	–0.18	–0.17	–0.18
C <sup>η</sup>	–0.13	–0.13	–0.13	–0.13
H <sup>γ</sup>	0.17	0.14	0.17	0.14
H <sup>λ</sup>	0.17	0.15	0.17	0.16

<sup>a</sup> e = charge of one electron.

attack. In addition, the band gap, calculated as HOMO–LUMO, can be used to evaluate the stability of the molecules and their reactivities in some reactions [5,57,58]. The plots of the Frontier molecular orbitals are shown in Fig. 3, which were obtained at B3LYP/6-31G\* level. As mentioned above, when AlPc is reduced the Al atom is projected out of the molecular plane. Analysis of the Frontier molecular orbitals helps to clarify this behavior. In the oxidized state, AlPc is a compound with a closed shell, that is, it presents all its electrons paired and, therefore, has multiplicity 1. As can be seen in Fig. 3, the HOMO orbital of the [AlPc]<sup>+</sup> is a  $\pi$  bonding orbital located entirely on the phthalocyanine ring, and it has no contribution in the region where the Al atom is located. When the [AlPc]<sup>+</sup> complex is reduced by adding an extra electron, the complex becomes an open shell system with multiplicity 2. In this case, the electrons  $\alpha$  and  $\beta$  should be separated in the calculation. So, two HOMO orbitals are calculated: HOMO- $\alpha$  and HOMO- $\beta$ . As can be seen in Fig. 3a, the HOMO- $\beta$  does not contribute to the Al–N<sup>α</sup> bond. However, the HOMO- $\alpha$  orbital is localized in the molecular region where the Al is attached to the phthalocyanine (see Fig. 3b). This orbital has a strong anti-bonding character between Al and nitrogen atoms. It turns out that placing an electron in this orbital decreases the bond order of the Al–N bond and, consequently, reduces the strength of this bond. This is the main reason that leads to the projection of the Al atom out of its molecular plane in the reduced state.

### 3.2. [(NO)AlPc]<sup>+</sup> and [(NO)AlPc]<sup>0</sup> complexes

As previously stated, NO is a molecule with broad pharmacological interest. However, it is very reactive and needs a carrier to take it to the biologically active site. Logically, this carrier cannot be toxic and, furthermore, should provide different lability for NO in different states of oxidation or excitation. As AlPc is easy to synthesize [59] and presents low toxicity it could, in principle, be used for this purpose. The calculation results presented in Table 1 show that the Al–NO bond length is 0.27 Å greater in the oxidized state than in the reduced state. This clearly suggests that the Al–NO bond is more labile in the oxidized state than in the reduced state, which is useful information in view of the purpose presented here. Note that the projection of the Al atom out of the plane in the [(NO)AlPc]<sup>0</sup> complex is 0.29 Å smaller than that calculated for the [(NO)AlPc]<sup>+</sup>. This suggests that the presence of the NO group in the reduced state helps to stabilize the complex. The main change that occurs in the molecular geometry of [AlPc]<sup>+</sup> when the NO is adsorbed by the Al atom is the displacement of 0.10 Å of the Al atom from the molecular plane.

Table 2 shows the calculated bond orders. The order of a bond is often associated with bond strength and is, in turn, related to bond length. Actually, bond orders decrease exponentially with increasing bond length [60]. The obtained bond order for the ON...AlPc bond in the [(NO)AlPc] is 0.49 for the reduced state and 0.22 for

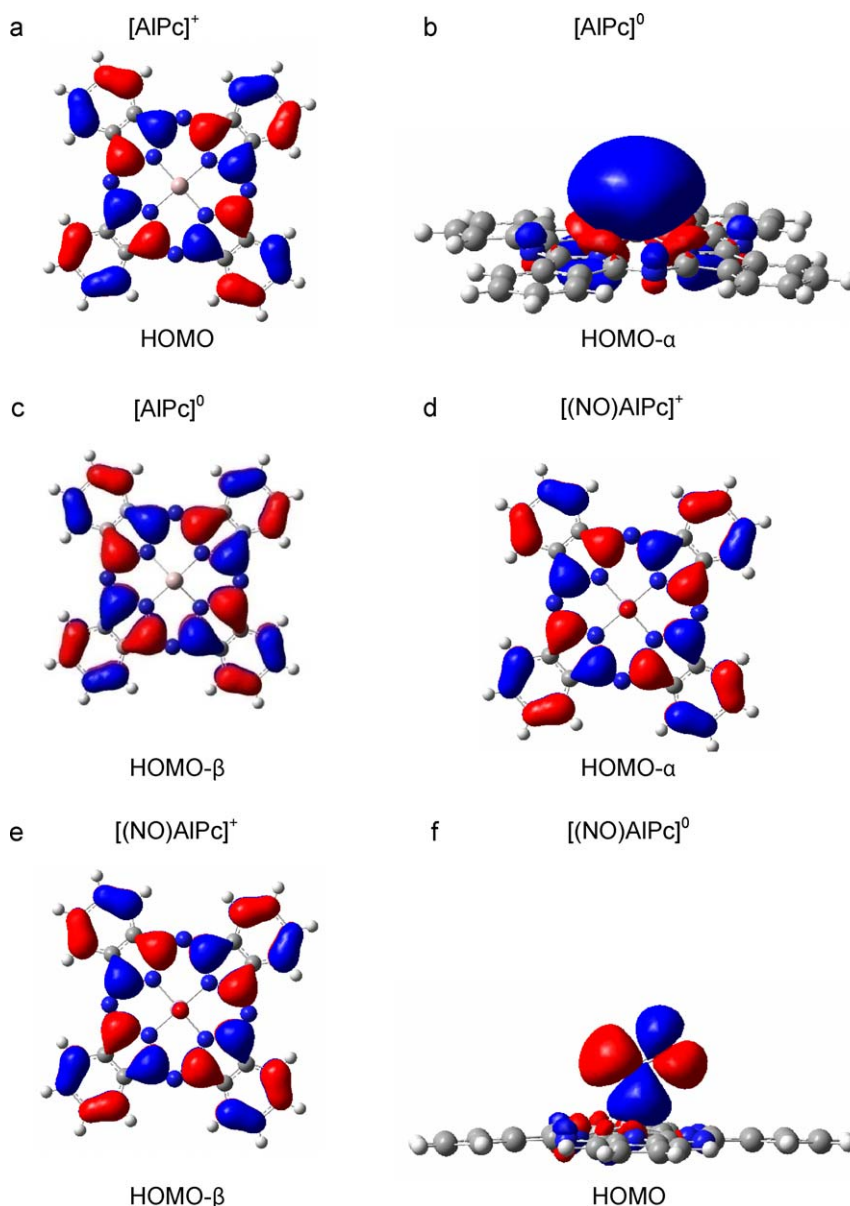
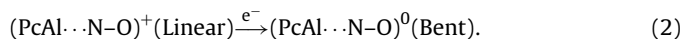


Fig. 3. Frontier molecular orbital for AlPc and (NO)AlPc in the reduced and oxidized states at B3LYP/6-31G\* level.

the oxidized state. These values explain the fact that the  $\text{ON} \cdots \text{AlPc}$  bond length is 0.27 Å greater in the oxidized state than in the reduced state. Therefore, we can infer that NO is stronger bonded to the Al atom in the reduced state than in the oxidized state. The  $\text{Al} \cdots \text{N}^\alpha$  bond order decreases from 0.37 for the oxidized state to 0.32 for the reduced state, which is justified considering the greater interaction of the NO group with aluminum in the reduced state. That increases the distance of the Al atom from the molecular plane in the reduced state when compared to the oxidized state (see Table 2).

The atomic partial charges derived from Mulliken analysis obtained at B3LYP/6-31G\* level are presented in Table 3. When NO is adsorbed by AlPc a strong redistribution of the electronic charges can be observed, principally on aluminum, oxygen and nitrogen of the NO group. The decrease in charge for these atoms from oxidized state to reduced state is 0.08, 0.15 and 0.24, respectively. As can be seen in Table 3, when [(NO)AlPc] is reduced 40% of the charge stays in the NO group, 8% stays in the Al atom and 52% goes to the phthalocyanine ring. This transference of charge to nitric oxide is closely related to variations in the angle  $\text{Al} \cdots \text{N}-\text{O}$ , since this angle

can assume two conformations, as either “bent” or “linear” [61]. The concentration of negative charge in the nitric oxide characterizes bent geometry ( $\text{Al} \cdots \text{N}-\text{O} = 120.42^\circ$ ) and the loss of electronic density in the same molecule and the fact that a weak interaction exists between the aluminum and NO characterizes linear geometry [62–66] as follows



The interaction strength between AlPc and NO gas can also be quantified calculating the bonding energy formation of the (NO)AlPc complex in its different oxidized states, as described. The energy calculations take into account the corrections for ZPVE and BSSE. The general reaction of the complex formation can be written as



The energy values obtained from the calculations for NO complexation with AlPc in the oxidized and reduced states are −4.96 kcal/mol and −33.77 kcal/mol, respectively (see Table 4).



**Table 4**

The calculated binding energies at B3LYP/6-31G\* level including the BSSE and ZPVE corrections.

Reaction of complex formation	Binding energy in kcal/mol
[AlPc] <sup>+</sup> + NO → [(NO)AlPc] <sup>+</sup>	−4.96
[AlPc] <sup>0</sup> + NO → [(NO)AlPc] <sup>0</sup>	−33.77

These values show that the NO molecule is stronger bonded to AlPc in the reduced state than in the oxidized state.

Analysis of the results in Table 5 shows a difference between the energies of the orbitals HOMO-α and HOMO-β (band gap energy) for the [AlPc]<sup>0</sup> complex, 1.55 eV. The difference between the energies of the orbitals HOMO-α and HOMO-β for the [(NO)AlPc]<sup>+</sup> complex is insignificant. Table 5 also shows a decrease in the band gap for the [AlPc] complex when reduced, and an inverse effect for the [(NO)AlPc] complex, with values for oxidized and reduced states; 1.95 eV, 0.54 eV for [AlPc] and 0.71 eV, 0.94 eV for [(NO)AlPc]. This fact is interesting, because the band gap variation is closely related to electric conductivity variation in the phthalocyanine complex [67], making the utilization of this compound as a chemical sensor possible.

### 3.3. Reactivity descriptors

From the results given above, it is seen that NO may complex with [AlPc]<sup>0</sup> and [AlPc]<sup>+</sup> forming the complexes [(NO)AlPc]<sup>0</sup> and [(NO)AlPc]<sup>+</sup>, of which the former is more stable in terms of energy, as can be seen in Table 4. In order to seek a possible explanation for these complexation phenomena we have also calculated the Fukui functions and applied the theory of hard-and-soft acid–base (HSAB) in the reactants. The statement that “soft likes soft” and “hard likes hard”, together with the idea that the higher the value of the Fukui function, the greater the reactivity, is also a very useful approach to explain the chemical reactivity of many chemical systems [68–74]. The determination of the specific sites at which the interaction between two chemical species take place is very important to elucidate the path and the products of a given reaction. As stated by Gázquez and Meñdez [75] the highest value of the Fukui function is, in general, associated with the most reactive site. In this work, we are especially interested in describing the interaction of NO with AlPc in different oxidation states (0,+1). According to the calculated data shown in Table 6, the highest Fukui function ( $f^0 = 0.541$ ) for nitric oxide is found in nitrogen and, in turn, this site governs a radical interaction. Silva et al. [27] have calculated the reactivity descriptor for the complexes [AlPc]<sup>0</sup> and [AlPc]<sup>+</sup>, and their results showed that the Fukui function ( $f^0$ ) for Al is 0.401 and 0.000, respectively. The highest value for Al of the complex [AlPc]<sup>0</sup> shows that the interaction of nitric oxide will occur preferentially with [AlPc]<sup>0</sup>, forming a bond. This result is in close agreement with geometric, electronic and energy data analyzed previously. Table 6 shows that NO can be considered as a hard acid and the results cal-

**Table 5**

Frontier molecular orbital energies calculated for AlPc and (NO)AlPc in the reduced and oxidized states at B3LYP/6-31G\* level. The orbital energies are in Hartree and ΔE in electron volts (eV).

	E (HOMO)	E (LUMO)	ΔE (eV)	Band gap (eV)
[AlPc] <sup>+</sup>	−0.29237	−0.22063	1.95	1.95
[AlPc] <sup>0</sup>	α-Orbital	−0.12693	0.54	0.54
	β-Orbital	−0.18384	2.12	
[(NO)AlPc] <sup>+</sup>	α-Orbital	−0.28968	0.72	0.71
	β-Orbital	−0.28957	1.14	
[(NO)AlPc] <sup>0</sup>	−0.14549	−0.11111	0.94	0.94

**Table 6**

Global hardness ( $\eta$ ) and softness ( $S$ ), and Fukui function  $f^0$  calculated at B3LYP/631G\* level of theory for nitric oxide (NO).

	$\eta$ (eV)	$S$ (eV)	$f^0$		
			N	O	Al
NO	12.915	0.077	0.541	0.303	–
*[AlPc] <sup>0</sup>	3.694	0.271	–	–	0.401
*[AlPc] <sup>+</sup>	4.161	0.240	–	–	0.000

Results obtained from Ref. [27].

culated by Silva et al. assume that aluminum phthalocyanine can also be considered as a hard acid; in this situation the global HSAB theory is not applicable.

## 4. Conclusions

In this work we have applied DFT to study theoretically the nature of the interaction between nitrogen oxides and AlPc, observing if AlPc can be employed as a selective chemical sensor for NO and as an NO carrier in biological systems. The calculation results using the exchange correlation functional B3LYP and basis set 6-31G\* show that the [AlPc]<sup>+</sup> complex has molecular symmetry belonging to the D<sub>4h</sub> point group, i.e., a planar structure, and the [AlPc]<sup>0</sup> complex has symmetry belonging to the C<sub>4v</sub> point group with the Al atom out of its molecular plane by about 0.6 Å. The change in the structure of the AlPc complex due to the oxidation state is attributed to the HOMO orbital. The HOMO orbital of the [AlPc]<sup>0</sup> complex is centered on the Al atom and it has an anti-bonding nature, which weakens the Al–N bonding, taking the Al atom out of its plane. The calculations show that the Al–NO bond length is 0.27 Å greater in the oxidized state than in the reduced state. The obtained bond order for the ON···AlPc bond in [(NO)AlPc] is 0.49 for the reduced state and 0.22 for the oxidized state. These values explain the fact that the ON···AlPc bond length is 0.27 Å greater in the oxidized state than in the reduced state. The calculated binding energies between NO and aluminum phthalocyanine agree with geometric data, with −4.96 kcal/mol in the oxidized state and −33.77 kcal/mol for the reduced state. The concentration of negative charge in the nitric oxide characterizes bent geometry, while the loss of electronic density and the fact that a weak interaction exists between the aluminum and NO characterizes linear geometry. For NO the highest calculated Fukui function ( $f^0 = 0.541$ ) is on N, showing that this site is the most favorable for the reaction to take place, and the Fukui function ( $f^0$ ) for Al is 0.401 for [AlPc]<sup>0</sup> and 0.000 for [AlPc]<sup>+</sup>. The highest value for Al of the complex [AlPc]<sup>0</sup> shows that the interaction of nitric oxide will occur preferentially with [AlPc]<sup>0</sup>, forming a bond. This result is in close agreement with geometric, electronic and energy data obtained from the calculations. These results clearly suggest that the Al–NO bond is more labile in the oxidized state than in the reduced state, which is useful information in view of the purpose presented here, indicating that aluminum phthalocyanine can be used as a selective chemical sensor or as a biomedical NO delivery agent.

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