

EOMT

Óscar's wonderful end of master's thesis

Óscar Iglesias González

April 23, 2020

Óscar's Room Editions

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Colophon

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The harmony of the world is made manifest in Form and Number, and the heart and soul and all the poetry of Natural Philosophy are embodied in the concept of mathematical beauty.

– D'Arcy Wentworth Thompson

Preface

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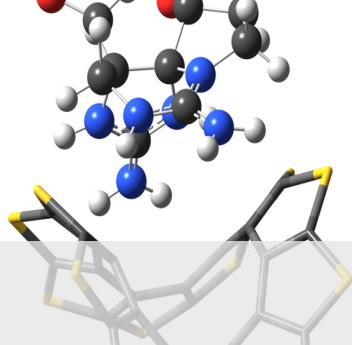
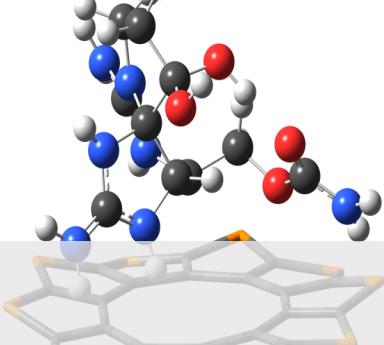
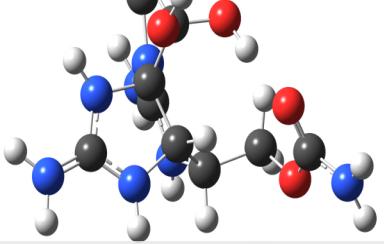
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1 Introduction

1.1 Marine toxins and saxitoxin

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1.2 The work up until now

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1.3 Pushing onwards

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```

137     self.bonds = []
138     for i in range(len(self.atoms)):
139         for j in range(i + 1, len(self.atoms)):
140             if i != j:
141                 d = np.linalg.norm(self.coords[i,:] - self.coords[j,:])
142                 if MIN_BOND_LENGTH <= d <= MAX_BOND_LENGTH:
143                     self.bonds.append({'atoms': (i, j),
144                                       'elements': (self.atoms[i],
145                                                    self.atoms[j]),
146                                       'distance': d})
147
148     def find_axis(self):
149         self.main_axis = best_fitted_plane(self.coords)

```

2 Computational methods and specifications

2.1 General techniques

Table 2.1: Computational techniques

| Calculation | Technique | Spec. | Functional | Basis set |
|------------------------|-----------|-------|------------|-----------|
| Geometry optimizations | DFT | | M06-2X | def2SVP |
| NICS calculations | DFT | GIAO | b3lyp | 6-31G* |

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2.2 Software

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2.3 Hardware

All of the calculations were performed using either the Centro de Supercomputación de Galicia’s (CESGA) infrastructures, or the proprietary cluster of the S3 research group.

S3’s cluster is composed of nodes that include 16 Intel®Xeon®CPU E5-2630 v3 2.40GHz cores and 60 GB of RAM.

CESGA’s



3 The sunflower molecules

3.1 Introduction and origin

The search for effective and interesting SERS substrates ended up leading us to a novel class of molecules researched and presented in the year 2006 by Chernichenko and his colleagues.[1] The first representative of this family, nicknamed as “sulflower”, is the ocatathio[8]circulene. This highly symmetric structure, which may be described as a form of carbon sulfide and as a belt of annulated thiophene cycles, is claimed to have great stability, high symmetry and unusual electronic properties.

From a synthetic point of view, sulflower also proved to be simple and straightforward to develop despite its complex appearance: starting from tetrathiophene, sulphurizing its free sites and acidifying it to get polythiol, and removing the excess sulfur by vacuum pyrolysis. This process allowed the team to achieve yields of 56% starting from commercially available reagents.

Interestingly, the team proposes that it could be possible to prepare materials with diverse electronic properties by using different types of heteroatoms and varying on the basic structure of the molecule. Such a statement made apparent the potential of this family of molecules: highly symmetrical, stable, surface-like structures with variable electronic behavior could act as suitable SERS substrates. This chapter is entirely dedicated to that premise: the study and characterization of sulflower and sulflower-like molecules, which from now on I will collectively refer to as “sunflowers”. By designing, generating and studying our own family of sunflowers, we will be contributing to characterize a novel and interesting group of molecules, and we may be able to identify an ideal SERS environment for STX.

3.2 Sunflower design

To start designing a family of molecules, first we must clearly state their defining pattern. For this purpose, we adopt Chernichenko et al.’s own proposal: “a novel class of heterolytic circulenes”. We start expanding the model by answering the question: are thiophene based circulenes with other than 8 rings stable enough to be worth considering? The answer is in the original paper itself. Figure 3.2, which was recreated to use our calculation level and adapt to the style of the document, shows that 8 ring structures are the most stable alongside 9. The details about this calculation are further explained in Section 3.3. However, considering their low relative energies and the fact that they have an even number of electrons (which would greatly simplify later calculations), 10 and 12 ring sunflowers were also chosen as part of the study.

[1]: Chernichenko et al. (2006), “Sulflower”: A New Form of Carbon Sulfide’

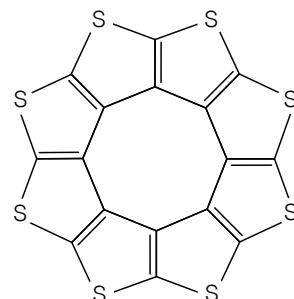


Figure 3.1: Structure of sulflower

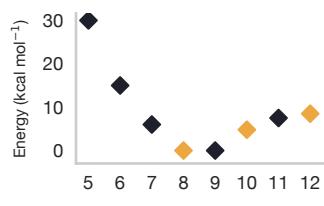


Figure 3.2: Strain of thiophenic circulenes with n rings

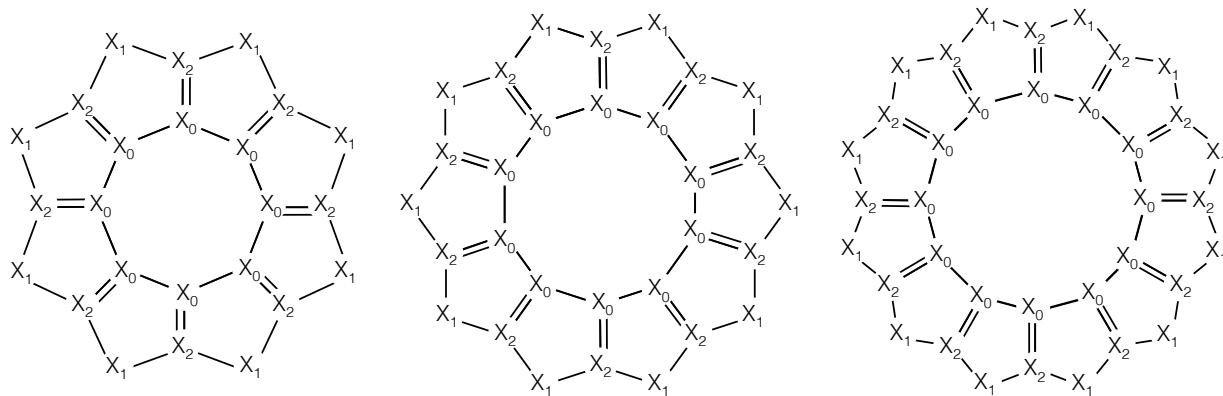


Figure 3.3: From left to right, general structures of the 8, 10 and 12 ring sunflowers

Table 3.1: Subset of the sunflower family that is going to be studied

| X_0 | X_1 | X_2 | number of rings | | |
|-------|-------|-------|-----------------|-------|-------|
| | | | 8 | 10 | 12 |
| C | S | C | S08 | S10 | S12 |
| C | Se | C | Se08 | Se10 | Se12 |
| C | As | C | As08 | As10 | As12 |
| C | As | N | AsN08 | AsN10 | AsN12 |
| C | P | C | P08 | P10 | P12 |
| C | P | N | PN08 | PN10 | PN12 |

Expanding upon this idea to allow for further heteroatom substitution, we ended up with the templates in Figure 3.3. The possibilities were numerous, but we settled for S, Se, As and P substitutions on X_1 sites, and N substitutions in some cases in X_2 sites. A full table detailing all of the structures that were generated and will comprise this study can be found in Table 3.1, as well as the short names or IDs that were given to each species based on its composition and number of petals for the sake of abbreviation.

3.3 Study of stability

Coordinate files for all of the designed sunflowers were created using 3D molecule modeling software. Then, they were optimized at the M06-2X/def2SVP calculation level.

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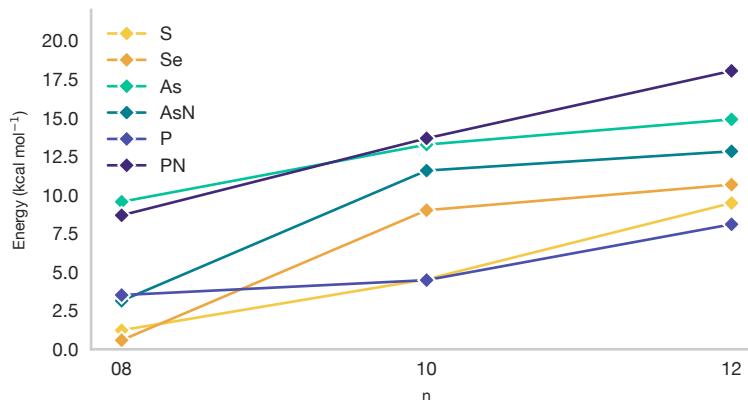


Figure 3.4: Strain energies of all of the studied sunflower groups

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3.4 Study of geometry

Using the output files from the previous step, specifically those from the initial optimization, all of the bond distances in all of the systems were extracted using Python. Then, the bonds were grouped by type: inner (I, bonds between X_0 atoms, which were carbon in all cases), middle (M, between X_0 and X_2 atoms, which were either C-C or C-N bonds), and outer (O, between X_2 and X_1 atoms). The mean and standard deviation (SD) of these groups was computed for all of the flowers. Additionally, thiophene-like pentagonal structures of the form displayed in Figure 3.5 were modeled and optimized, and their bond length data was compared with the rest and presented in Table 3.2.

How is this information useful? In the first place, it allows us to easily compare the average length of each bond type as the number of units increases. More interestingly, it serves as a way to assess the nature of each bond group. Take the inner C-C bonds. In all cases, the average length lies between the usual values for single and double C-C bonds,¹ an information that immediately suggests us that the flowers might be conjugated systems with π electron delocalization. However, it could also be possible that there were equal amounts of single and double bonds, and that these apparently conjugated bond lengths were just a the result of a lousy statistical approximation. That's why the SD metric was also computed. Groups with a relatively high SD such as the I bonds of As08, As12, P08 and P12 are actually composed of longer and shorter bonds, and it's likely that their π electrons aren't delocalized. On the other hand, groups with small SD values are more likely to correspond to conjugated systems, which may be stabilized by electron delocalization. This concept of bond length equalization and conjugation may be tied to that of aromaticity, where equalized C-C bonds could be a sign of it, and uneven ones could indicate non aromaticity or antiaromaticity.^[2] This topic will be covered in greater detail in Section 3.5.

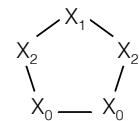


Figure 3.5: Thiophene-like structure template (hydrogen is added to adjust for neutrality as needed)

1: 1.54 Å for single and 1.34 Å for double bonds [add reference](#)

[2]: Chen et al. (2005), 'Nucleus-Independent Chemical Shifts (NICS) as an Aromaticity Criterion'

Table 3.2: Bond length statistics for each studied species, units are Å

| | | I (X_0-X_0) | | M (X_0-X_2) | | O (X_1-X_2) | |
|-----|------|-----------------|-------|-----------------|-------|-----------------|-------|
| | | mean | std | mean | std | mean | std |
| S | ring | 1.429 | - | 1.367 | 0.000 | 1.719 | 0.000 |
| | 08 | 1.423 | 0.000 | 1.377 | 0.000 | 1.754 | 0.000 |
| | 10 | 1.482 | 0.000 | 1.399 | 0.000 | 1.712 | 0.000 |
| | 12 | 1.466 | 0.004 | 1.389 | 0.000 | 1.732 | 0.004 |
| Se | ring | 1.434 | - | 1.363 | 0.000 | 1.857 | 0.000 |
| | 08 | 1.454 | 0.000 | 1.385 | 0.000 | 1.865 | 0.000 |
| | 10 | 1.478 | 0.003 | 1.389 | 0.000 | 1.861 | 0.004 |
| | 12 | 1.466 | 0.007 | 1.381 | 0.000 | 1.877 | 0.005 |
| As | ring | 1.468 | - | 1.354 | 0.000 | 1.918 | 0.000 |
| | 08 | 1.434 | 0.050 | 1.448 | 0.000 | 1.859 | 0.008 |
| | 10 | 1.436 | 0.000 | 1.454 | 0.001 | 1.856 | 0.001 |
| | 12 | 1.435 | 0.042 | 1.446 | 0.002 | 1.867 | 0.007 |
| AsN | ring | 1.495 | - | 1.283 | 0.000 | 1.854 | 0.000 |
| | 08 | 1.434 | 0.000 | 1.361 | 0.000 | 1.858 | 0.000 |
| | 10 | 1.450 | 0.001 | 1.364 | 0.001 | 1.856 | 0.004 |
| | 12 | 1.440 | 0.004 | 1.357 | 0.001 | 1.873 | 0.006 |
| P | ring | 1.467 | - | 1.359 | 0.000 | 1.794 | 0.001 |
| | 08 | 1.410 | 0.048 | 1.445 | 0.000 | 1.764 | 0.006 |
| | 10 | 1.431 | 0.000 | 1.471 | 0.000 | 1.736 | 0.000 |
| | 12 | 1.429 | 0.045 | 1.462 | 0.002 | 1.747 | 0.005 |
| PN | ring | 1.485 | - | 1.293 | 0.000 | 1.707 | 0.000 |
| | 08 | 1.404 | 0.000 | 1.364 | 0.000 | 1.752 | 0.000 |
| | 10 | 1.448 | 0.000 | 1.385 | 0.000 | 1.715 | 0.001 |
| | 12 | 1.435 | 0.002 | 1.378 | 0.001 | 1.732 | 0.004 |

3.5 Study of aromaticity

Aromaticity is a property of molecules that have a ring or a chain of resonance bonds that increases their stability. Initially associated with benzene, it's typically found in flat ring structures (although there are other varieties such as homoaromatic and three-dimensional aromatic systems).

Nucleus-Independent Chemical Shift (NICS)

NICS

The basics of NICS

As π electrons in aromatic systems have free circulation, an external magnetic field perpendicular to the main plane of the system is able to induce a ring current. The NICS technique as a probe for aromaticity is based on the idea that NMR chemical shifts are influenced by said ring currents, as a consequence of Ampère's law. Ring currents generate their own magnetic field, which will weaken or strengthen the effect of the

external field resulting in decreased or increased shifts. Aromatic systems will experience shielding on the inside of the ring and deshielding on the outside. Antiaromatic systems will experience the opposite.

A custom solution for non-planar molecules

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AICD

The basics of AICD

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Application and comparison of results

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3.6 Spectroscopic characterization

Vibrational spectroscopy

Raman spectra

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Decomposition of key modes

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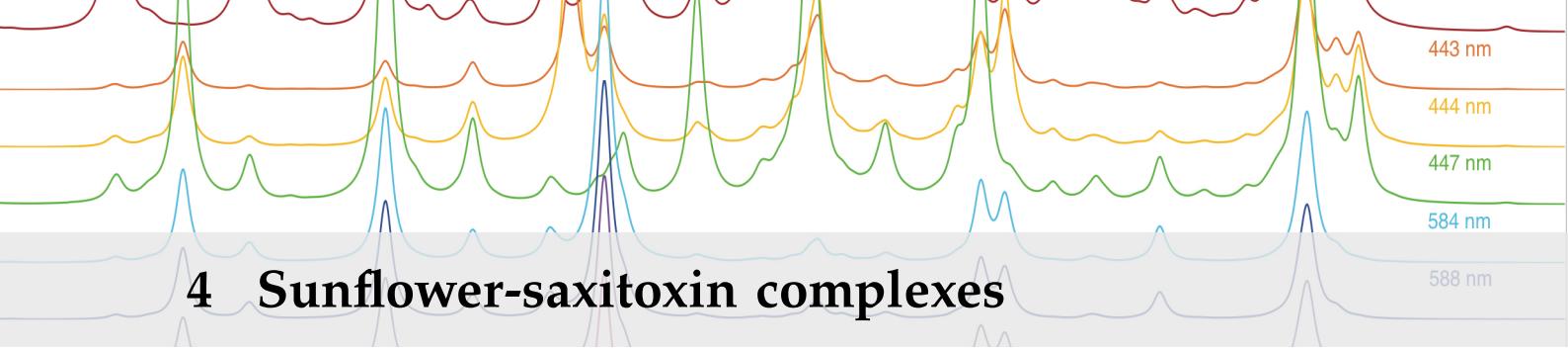
VEDA

Hello, here is some text without a meaning. This text should show what a printed text will look like at this place. If you read this text, you will get no information. Really? Is there no information? Is there a difference between this text and some nonsense like "Huardest gefburn"? Kjift – not at all! A blind text like this gives you information about the selected font, how the letters are written and an impression of the look. This text should contain all letters of the alphabet and it should be written in of the original language. There is no need for special content, but the length of words should match the language.

Electronic spectroscopy

UV spectra

Hello, here is some text without a meaning. This text should show what a printed text will look like at this place. If you read this text, you will get no information. Really? Is there no information? Is there a difference between this text and some nonsense like "Huardest gefburn"? Kjift – not at all! A blind text like this gives you information about the selected font, how the letters are written and an impression of the look. This text should contain all letters of the alphabet and it should be written in of the original language. There is no need for special content, but the length of words should match the language.



4 Sunflower-saxitoxin complexes

Having obtained a general characterization of the sunflower-type molecules, it's time to get back to the problem at hand and start looking into how they can be applied.

Let's reintroduce the molecule that motivated this whole study: saxitoxin (STX). For the purposes of this study, the STX structure features two guanidinium moieties (which are protonated due to the simulation of acidic conditions), two hydroxyl, and one carbamate group as it can be seen in Figure 4.1.

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4.1 Spectroscopic study of lone STX

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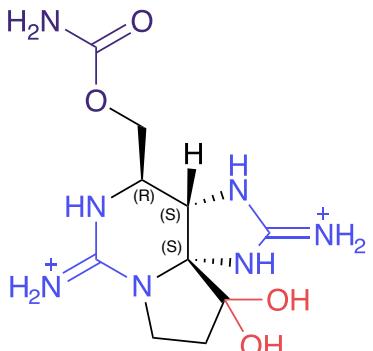


Figure 4.1: Structure of STX

the original language. There is no need for special content, but the length of words should match the language.

4.2 Study of adsorption

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Sampling and optimization

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Maxwell-Boltzmann statistics

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Basis Set Superposition Error correction

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4.3 Study of non-covalent interactions

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4.4 Study of UV behavior

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General UV spectroscopy

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Charge transfer analysis

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4.5 Resonance Raman

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Generation and comparison of spectra

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Combined resonance graphs

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Final selection

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APPENDIX

A Some more blindtext

Hello, here is some text without a meaning. This text should show what a printed text will look like at this place. If you read this text, you will get no information. Really? Is there no information? Is there a difference between this text and some nonsense like "Huardest gefburn"? Kjift – not at all! A blind text like this gives you information about the selected font, how the letters are written and an impression of the look. This text should contain all letters of the alphabet and it should be written in of the original language. There is no need for special content, but the length of words should match the language.

Bibliography

Here are the references in citation order.

- [1] Konstantin Yu. Chernichenko et al. "Sulflower": A New Form of Carbon Sulfide'. In: *Angew. Chem. Int. Ed.* 45 (2006), pp. 7367–7370 (cited on page 7).
- [2] Zhongfang Chen et al. 'Nucleus-Independent Chemical Shifts (NICS) as an Aromaticity Criterion'. In: *Chem. Rev.* 118 (2005), pp. 3842–3888 (cited on page 9).

Notation

The next list describes several symbols that will be later used within the body of the document.

c Speed of light in a vacuum inertial frame

h Planck constant

Greek Letters with Pronunciation

| Character | Name | Character | Name |
|--------------------|---------------------------|----------------------|----------------------------------|
| α | alpha <i>AL-fuh</i> | ν | nu <i>NEW</i> |
| β | beta <i>BAY-tuh</i> | ξ, Ξ | xi <i>KSIGH</i> |
| γ, Γ | gamma <i>GAM-muh</i> | \omicron | omicron <i>OM-uh-CRON</i> |
| δ, Δ | delta <i>DEL-tuh</i> | π, Π | pi <i>PIE</i> |
| ϵ | epsilon <i>EP-suh-lon</i> | ρ | rho <i>ROW</i> |
| ζ | zeta <i>ZAY-tuh</i> | σ, Σ | sigma <i>SIG-muh</i> |
| η | eta <i>AY-tuh</i> | τ | tau <i>TOW (as in cow)</i> |
| θ, Θ | theta <i>THAY-tuh</i> | υ, Υ | upsilon <i>OOP-suh-LON</i> |
| ι | iota <i>eye-OH-tuh</i> | ϕ, Φ | phi <i>FEE, or FI (as in hi)</i> |
| κ | kappa <i>KAP-tuh</i> | χ | chi <i>KI (as in hi)</i> |
| λ, Λ | lambda <i>LAM-duh</i> | ψ, Ψ | psi <i>SIGH, or PSIGH</i> |
| μ | mu <i>MEW</i> | ω, Ω | omega <i>oh-MAY-guh</i> |

Capitals shown are the ones that differ from Roman capitals.

