EOMT

Óscar's wonderful end of master's thesis

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Óscar's Room Editions

EOMT

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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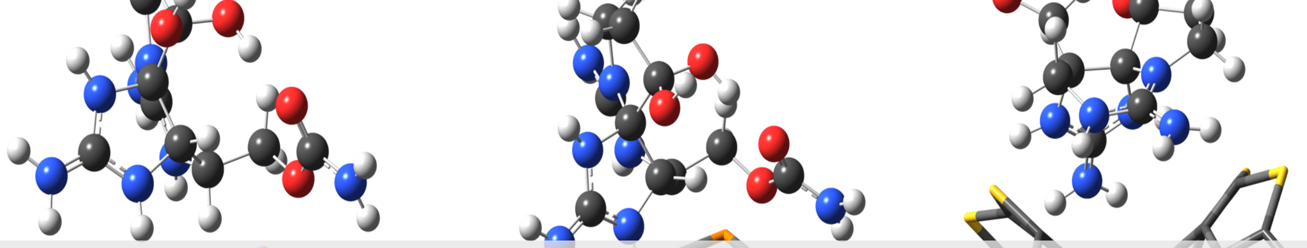

1 Introduction

1.1 Introduction to marine toxins and saxitoxin (STX)

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1.2 The work up until now

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1.3 Pushing onwards

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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	def2TZVPP
NICS calculations	DFT	GIAO	b3lyp	base

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2.2 Software

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2.3 Hardware

All of the calculations were perfomed using either the Centro de Supercomputación de Galicia’s (CESGA) infraestructures, or the propietary 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.

[1]: Chernichenko et al. (2006), '"Sulflower": A New Form of Carbon Sulfide'

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 acidificating ot get polythiol, and removing the excess sulfur by vacuum pyrolysis. This allowed the team to achieve yields of 56% starting from commercially available reagents.

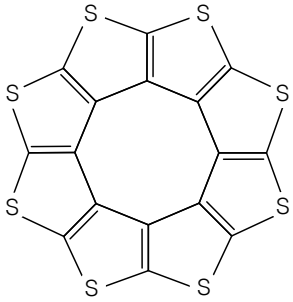

Figure 3.1: Structure of sulflower

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. 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.

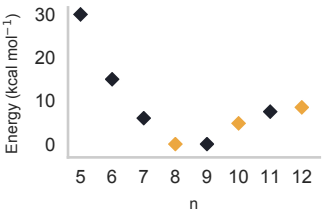

Figure 3.2: Strain of thiophenic circulenes with n rings

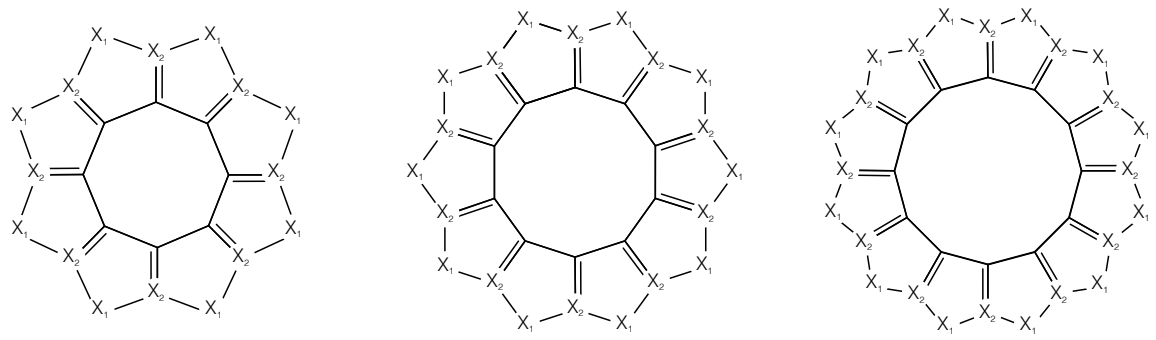

Figure 3.3: From left to right, general structures of the 8, 10 and 12 ring sunflowers

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

		n		
X_1	X_2	8	10	12
S	C	S08	S10	S12
Se	C	Se08	Se10	Se12
As	C	As08	As10	As12
As	N	AsN08	AsN10	AsN12
P	C	P08	P10	P12
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 flowers were created using 3D molecule modeling software. Then, they were optimized at the M06-2X/def2SVP calculation level.

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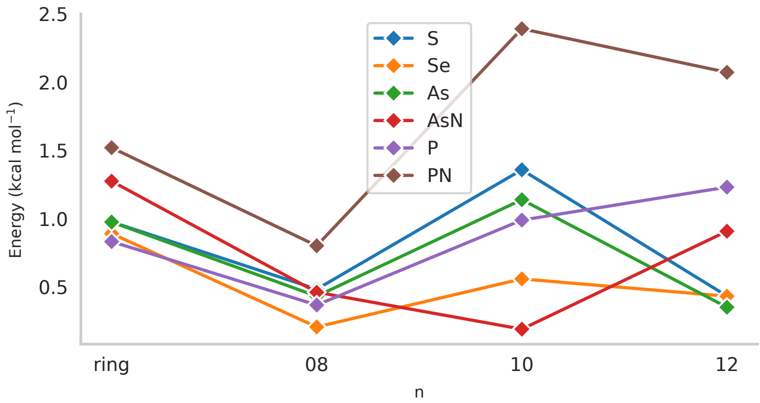

Figure 3.4: Relative energies of the defined sunflower families with respect to the most stable species

3.4 Study of geometry

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Table 3.2: Bond length statistics for each studied species

		C-C		$C-X_2$		X_1-X_2	
		mean	std	mean	std	mean	std
S	ring	0.000	0.000	0.000	0.000	0.000	0.000
	08	0.000	0.000	0.000	0.000	0.000	0.000
	10	0.000	0.000	0.000	0.000	0.000	0.000
	12	0.000	0.000	0.000	0.000	0.000	0.000
Se	ring	0.000	0.000	0.000	0.000	0.000	0.000
	08	0.000	0.000	0.000	0.000	0.000	0.000
	10	0.000	0.000	0.000	0.000	0.000	0.000
	12	0.000	0.000	0.000	0.000	0.000	0.000
As	ring	0.000	0.000	0.000	0.000	0.000	0.000
	08	0.000	0.000	0.000	0.000	0.000	0.000
	10	0.000	0.000	0.000	0.000	0.000	0.000
	12	0.000	0.000	0.000	0.000	0.000	0.000
AsN	ring	0.000	0.000	0.000	0.000	0.000	0.000
	08	0.000	0.000	0.000	0.000	0.000	0.000
	10	0.000	0.000	0.000	0.000	0.000	0.000
	12	0.000	0.000	0.000	0.000	0.000	0.000
P	ring	0.000	0.000	0.000	0.000	0.000	0.000
	08	0.000	0.000	0.000	0.000	0.000	0.000
	10	0.000	0.000	0.000	0.000	0.000	0.000
	12	0.000	0.000	0.000	0.000	0.000	0.000
PN	ring	0.000	0.000	0.000	0.000	0.000	0.000
	08	0.000	0.000	0.000	0.000	0.000	0.000
	10	0.000	0.000	0.000	0.000	0.000	0.000
	12	0.000	0.000	0.000	0.000	0.000	0.000

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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 techinque as a probe for aromaticity is based on the idea that NMR chemical shifts are influenced by said ring currents, as a consecuence 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

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Electronic spectroscopy

UV spectra

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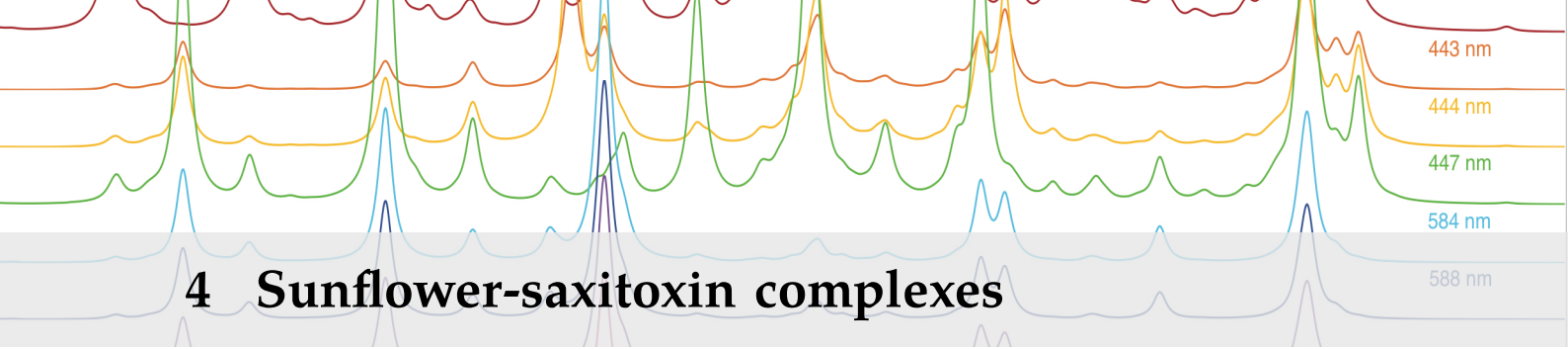

4 Sunflower-saxitoxin complexes

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.

4.1 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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4.2 Study of non-covalent interactions

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4.3 Study of UV behavior

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General UV spectroscopy

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Charge transfer analysis

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4.4 Resonance Raman

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Generation and comparison of 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.

Combined resonance graphs

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.

Final selection

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.

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 5).

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 Pronounciation

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

Capitals shown are the ones that differ from Roman capitals.