

EOMT

Óscar's wonderful end of master's thesis

Óscar Iglesias González

March 31, 2020

Óscar's Room Editions

EOMT

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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

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.

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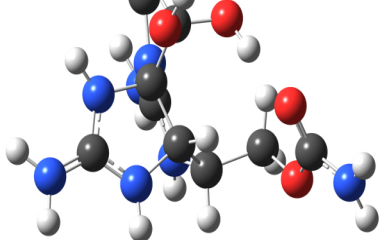
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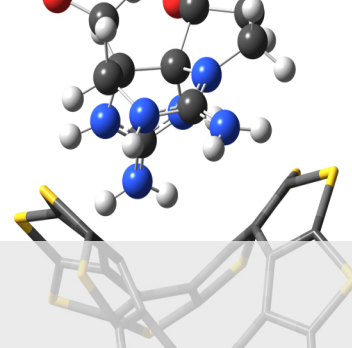
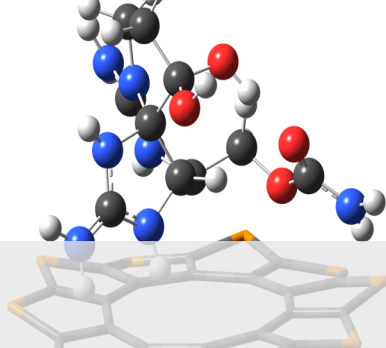
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1 Introduction



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

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.

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

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.

2.3 Hardware

All of the calculations were performed using either the Centro de Supercomputación de Galicia’s (CESGA) infraestructures, 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 be very stable and straightforward to synthesize. More interestingly, the team states 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. 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 may be able to identify a suitable SERS substrate that satisfies our requirements.

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

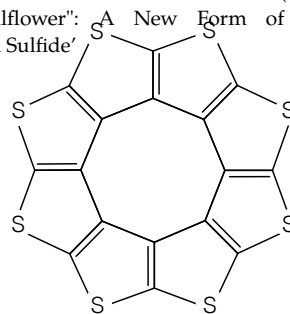


Figure 3.1: Structure of sulflower

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.

Expanding upon this idea to allow for further heteroatom substitution, we ended up with the templates in Figure 3.3.

X_1	X_2	n		
		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

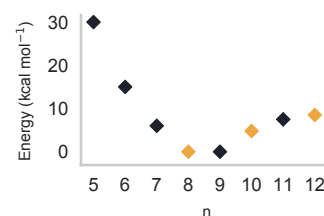


Figure 3.2: Strain of thiophenic circulenes with n rings

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

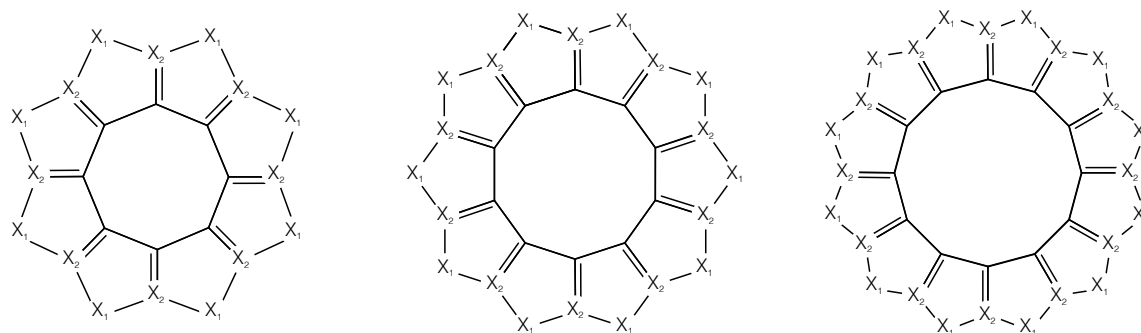


Figure 3.3: From left to right, general structures of the 8, 10 and 12 ring sunflowers

3.3 Study of geometry

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3.4 Study of aromaticity

Aromaticity is

Nucleus-Independent Chemical Shift (NICS)

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The basics of NICS

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

A custom solution for non-planar molecules

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AICD

The basics of AICD

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.

Application and comparison of results

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3.5 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

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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

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.

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

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Combined resonance graphs

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Final selection

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APPENDIX

A Some more blindtext

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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 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-uh</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.

