

EOMT

# **Óscar's wonderful end of master's thesis**

Óscar Iglesias González

May 18, 2020

CC Ediciones, Oscar's Room HQ

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What, that's impossible? Wait, how? How is this sunflower so chill. How, that's impossible, he can't be this chill. He is so chill, I can't believe it.

– Unknown



# 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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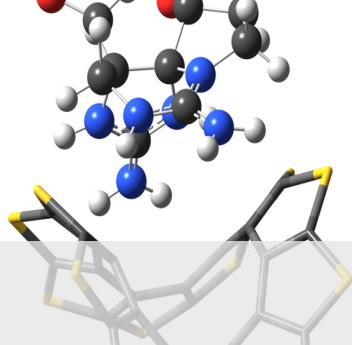
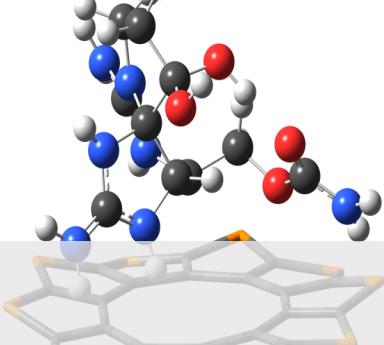
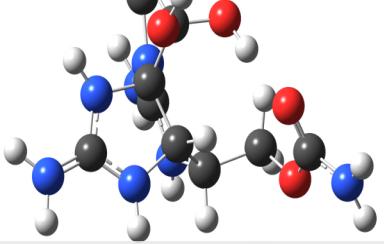
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# 1 Introduction

## 1.1 Marine toxins and saxitoxin

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. 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. 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.

## 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 Methods and techniques

Throughout this work, many different computational methods and techniques were employed in order to carry out a diverse set of studies. Some of them, the ones that are the most relevant to the flow of the work, are specifically explained and developed in detail in their own sections. Others, however, are deemed to be more of a general character, already well known within the field, or unimportant for the understanding of the main ideas of this thesis. This section is meant to serve as an overview of the methodology, specifications and theory behind the whole study, and also to provide explanations for that less special set of techniques. This part may be skimmed and consulted at a later time, or even skipped entirely, as the rest of the work is presented in such a way that can be followed without deep knowledge of the subjects that are explained here.

#### Calculation level

All of the electronic structure calculations were performed using Density Functional Theory (DFT) in the Kohn-Sham formulation. Specifically, the functional of choice was Minnesota's M06-2X.<sup>[1]</sup> M06-2X is a highly parametrized hybrid meta-GGA functional that features a 54 % of Hartree-Fock exchange. It was chosen because it has been extensively trained to perform well in a variety of contexts that include thermochemistry, the study of non covalent interactions, and vibrational and electronic spectroscopy. While the molecules discussed in the work are novel and have not been previously characterized, it's expected that their chemistry and their spectroscopic behavior aren't out of the ordinary. Therefore, it should be possible to describe them properly and efficiently with such a functional.

As for the basis functions, the set of choice was Weigend and Ahlrichs' def2-SVP.<sup>[2]</sup> def2-SVP is of split valence set and includes polarization functions, but is overall a fairly small set. However, it has been deemed sufficiently extense to obtain accurate geometry optimizations, and qualitatively good energies and spectra.

Considering the size of the systems of the study, the large amount of planned computations, the available computational resources, and the actual accuracy needs of the project, the M06-2X and def2-SVP calculation level was considered appropriate.

[1]: Zhao et al. (2008), 'The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals'

[2]: Weigend et al. (2005), 'Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy'

## Geometry optimization

The optimization of the geometry of a molecule is a crucial part of any computational modeling. At its core, it's a process where the geometry of a system gets iteratively modified (and its energy gets calculated at each step) with the aim of reaching a stationary point on its potential energy surface. In the case of this work, these optimizations are always minimizations as we just look for energy minima. In Gaussian, our electronic structure computation software of choice, these calculations are carried out using the Berny algorithm in its GEDIIS<sup>[3]</sup> implementation.

<sup>[3]</sup>: Li et al. (2006), 'Energy-represented DIIS within a hybrid geometry optimization method'

## Magnetic shielding computation

GIAO method. 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 transition study

TD-DFT. 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.

## Vibrational analysis

Vibrational normal modes. Infrared and Raman modes. Focus on only Raman. 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.

## Normal mode decomposition

**Internal modes calculation.** 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.

## Raman intensity calculation

?? 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.

## Resonance Raman

?? 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.

## Surface-enhanced Raman Spectroscopy

**Amplification effect nature.** 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.

### Spectra envelope calculation

Preexponential and sigma terms for UV. And for Raman 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.

## 2.2 Software

The software used to perform all of the calculations and tasks was varied.

## 2.3 Technique and software overview

**Table 2.1:** Computational techniques

Calculation	Technique	Spec.	Functional	Basis set	Software
Geometry optimizations	DFT		M06-2X	def2SVP	Gaussian
Surface generation					nics.py
NICS calculations	DFT	GIAO	b3lyp	6-31G*	Gaussian
Raman spectra generation	DFT		M06-2X	def2SVP	Gaussian
UV spectra generation	TD-DFT		M06-2X	def2SVP	Gaussian

## 2.4 Hardware

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

CESGA's supercomputer, FinisTerrae-II (FTII), is a Bull ATOS bullx machines that features 320 computation nodes, 7712 cores, 44 544 GB of RAM, and 750 000 GB of storage capacity. All of the calculations carried out at FTII were performed in standard nodes, utilizing 12 cores at a time, and 60 GB of RAM. These nodes include each 2 Intel®Xeon®E5-2630 v3 2.50 GHz processors with 24 cores total, and 128 GB of RAM.

S3's cluster is composed of nodes that feature 16 cores running on Intel®Xeon®E5-2630 v3 2.40 GHz processors, and 64 GB of RAM.

Smaller calculations such as input file generation, output parsing, surface estimation, graph representation... were carried out in the author's personal computer.



## 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.<sup>[4]</sup> 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 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.

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

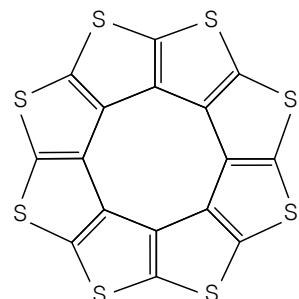


Figure 3.1: Structure of sulflower

### 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. The details about this calculation are further explained in Section 3.4. 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.

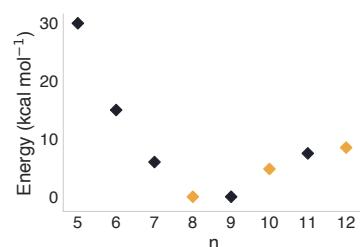
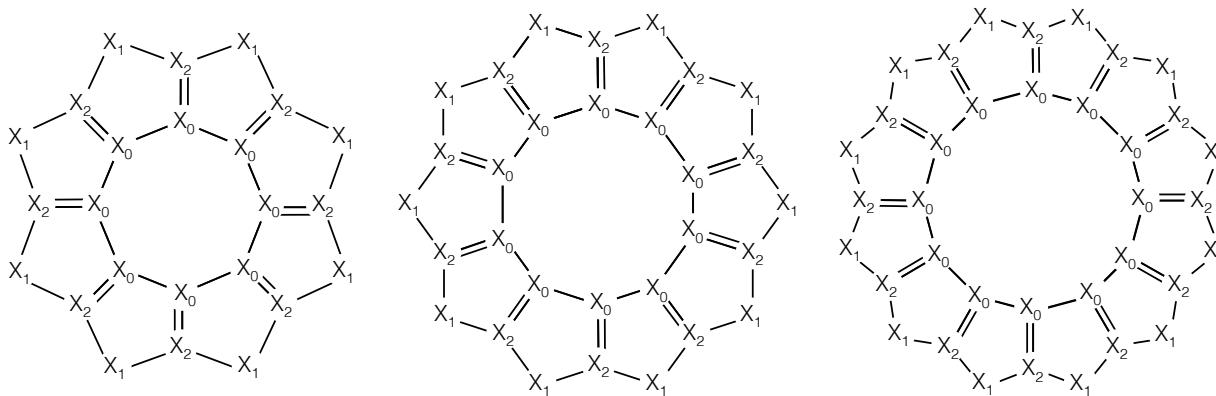


Figure 3.2: Strain of thiophenic circulenes with n rings



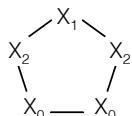
**Figure 3.3:** From left to right, general structures of the 8, 10 and 12 ring sunflowers

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

$X_0$	$X_1$	$X_2$	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.

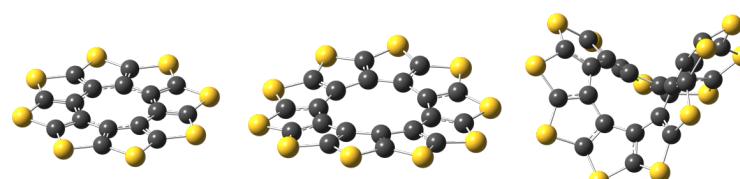
### 3.3 Study of geometry



**Figure 3.4:** Thiophene-like structure template (hydrogen is added to adjust for neutrality as needed)

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.

Using the output files for these calculations, 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



**Figure 3.5:** Shape of optimized S08, S10 and S12, from left to right (note the progressive increase in their deviation from planarity)

flowers. Additionally, thiophene-like pentagonal structures of the form displayed in Figure 3.4 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,<sup>1</sup> an information that immediately suggests us that the flowers might be conjugated systems with  $\pi$  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 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  $\pi$  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.<sup>[5]</sup> This topic will be covered in greater detail in Section 3.5.

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

[5]: 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

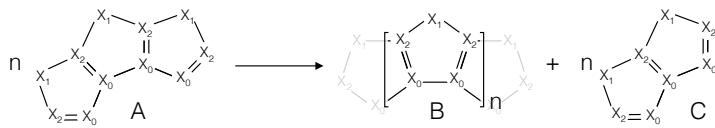
### 3.4 Study of stability

Using the output files from the previous step, specifically those from the initial optimization, calculations related to the energies of the flowers were performed in order to assess their stabilities.

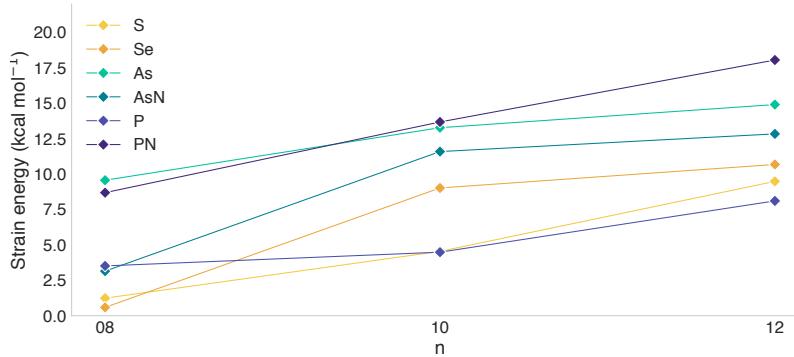
#### Ring strain

Ring strain may be defined as a kind of instability that arises when angles of the bonds in a cyclic molecule deviate from their optimal values, which they would be able to adopt if they weren't coiled in the shape of a ring. The energy associated to this phenomenon can serve as a way to compare the stabilities of flowers with different numbers of petals, as it was done in the original paper and reproduced in Figure 3.2. Its calculation relies on the design of an homodesmotic reaction. What does this mean? In a homodesmotic reaction, the number of atoms and the type of hybridizations in the products are the same as in the reactants. Our goal is to devise a chemical equation where the strained structure appears in only one of its sides and the rest of the chosen molecules don't present any stray effects.<sup>[6]</sup> If we manage to create such an equation, the reaction

[6]: Vidal-Vidal et al. (2005), 'Nitrogen Doped Nanohoops as Promising CO<sub>2</sub> Capturing Devices'



**Figure 3.6:** Homodesmotic reaction used to calculate strain energies



energy will correspond to the strain, as the rest of the components of the energy should nullify themselves between the two sides of the reaction.

In this case, apart from the sunflower structure B, the equations that were designed included molecules A and C, non-cyclic structures composed of 3 and 2 petals. By following this reaction, which is fully displayed in Figure 3.6, the strain energy was calculated as shown in Equation 3.1.

This calculation, which is the one that was used to generate the previous sunflower stability curve Figure 3.2, was applied to all of the sunflowers of the study, and the resulting strain energies are presented in Figure 3.7. As it can be seen, the strain energies always increase with the number of petals (as it's the case for the original sunflower series). However, it may be noted that they increase following slightly different tendencies. Notable examples are the P family, where the 8 and 10 petal species have very similar strains; and the Se, As and AsN families, where the energies of the 10 and 12 petal structures are very close. These energy values are an useful indication of the relative strains of the different species within a family, and an estimation of their stabilities with respect to the original sunflower. Nevertheless, it should be kept in mind that this calculation is an approximation, and that the values of the so called strain energy might be accounting for other effects such as conjugation stabilization or repulsion between the heteroatoms.

$$E_{\text{strain}} = \frac{E_B + nE_C - nE_A}{n} \quad (3.1)$$

**Figure 3.7:** Strain energies of all of the studied sunflower groups

## 3.5 Study of aromaticity

Aromaticity is a property related to molecules that contain a ring or a chain of resonance bonds that increases their stability. It's typically found in flat ring structures, although the definition has been discussed and expanded since its initial association to benzene,[7] and there are other varieties such as annulenic, azulenic, inorganic, homoaromatic, three-dimensional,  $\sigma$ -electron, and even metallic electron aromaticity.[5] Considering their ringed structure and possibly high conjugation, we wondered if the sunflowers could present any kind of aromatic tendencies. Having already studied their degree of bond length equalization in

[7]: Faraday (1825), 'On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat', Chen, et al. (2005), 'Nucleus-Independent Chemical Shifts (NICS) as an Aromaticity Criterion'

Section 3.3, we set out to assess their aromaticity from the point of view of their magnetic properties.

## Nucleus-Independent Chemical Shift (NICS)

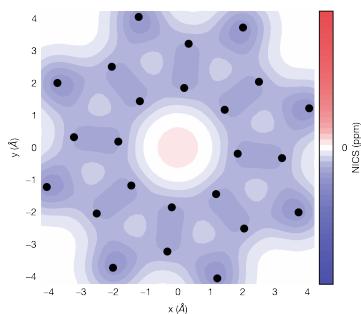
[8]: Ragué Schleyer et al. (1996), 'Nucleus-Independent Chemical Shifts: A Simple and Efficient Aromaticity Probe'

Since its introduction in 1996 by Schleyer et al.[8], NICS has become the most popular and widely used technique to estimate aromaticity in a quantitative way. It's based on the study of electronic ring currents. As the electrons in the possibly-aromatic systems have a certain degree of free circulation, an external magnetic field perpendicular to the main plane of the system is able to induce a ring current. Said ring currents generate their own magnetic field, which can weaken or strengthen the effect of the external field, resulting in decreased or increased NMR chemical shifts. Aromatic systems will experience shielding on the inside of the ring and deshielding on the outside. Antiaromatic systems will experience the opposite.

### The basic application of NICS

NICS is usually applied to single rings, and quantified by computing the absolute magnetic shielding at key locations. This key location is usually one of the following: the center of the ring (calculated as the non-weighted mean of the positions of the heavy atoms), several points along a central axis perpendicular to the plane of the ring (calculated trivially in planar rings as the plane that passes through any three ring atoms), at several points on a grid perpendicular to the plane of the ring, or as three dimensional isosurfaces using dense grids.

### A custom solution for non-planar molecules



**Figure 3.8:** Custom NICS technique applied to the original 8 petal sunflower molecule as a sample of the legacy approach

As seen in Figure 3.5 in Section 3.3, 8 petal sunflowers are perfectly planar. In previous studies, NICS calculations on flat grids parallel to their planes were applied with success. All of the points of the grid were equidistant to the plane of the molecule to be able to properly compare their values (the magnitude of the magnetic shielding decreases the farther away from the molecule that it is measured). The positive values of the magnetic shielding were plotted in red, and the negative ones in blue, which overlaid over the atoms of the flower, resulted in graphs like Figure 3.8. However, 10 and 12 petal sunflowers have bended and warped shapes, and the "general plane" of the molecule is no longer a plane. In order to translate the old method, a new approach was developed and applied. The idea of extending a grid of points over the surface of the system and plotting it as a 2D projection is maintained, but what is exactly the surface of a non planar molecule, and how can it be generalized for non planar molecules?

Defining the concept of "general surface" for a warped ring is a tricky task, but we've set on the following description: a 3D surface that is equidistant to all of the heavy atoms of a molecule and to all of the middle points of their bonds, and that follows a smooth and intuitive tendency in the places where are neither atoms nor bonds. A general surface could be loosely thought of as a blanket that was being draped over a physical

molecular model of the system, sitting on the places where there are balls and sticks, and covering the empty spaces smoothly without caving in.

To mathematically model such an idea, several approaches were evaluated and tested,<sup>2</sup> but in the end, the method was based on linearly combining a set of simple 3D cartesian functions.

This idea was born while thinking about the curvature of the largest sunflowers. "This Se10 molecule looks like it has the shape of a saddle."<sup>3</sup> What if we could find the precise parameters for a saddle that adjusted to the shape of this molecule?" This concept was expanded to include a wider variety of molecules and shapes: there's a limit to the angles and deformations that a ring in a molecule can display... so therefore, it should be possible to get a decent approximation to any molecular surfaces by combining and fine tuning a selection of common 3D shapes in the form of functions. The remaining question is... how can we find which 3D functions should be used, and what coefficients should be assigned to them? The functions were picked out by hand, and will later be enumerated and justified. The coefficients, however, had to be calculated somehow. Our solution, which will be fully explained hereunder, relies upon the core concepts of statistical learning.

First off, we start with just the coordinate file of the optimized structure of the studied molecule. We will use Se10 as an example. This file should contain the position of each of the atoms in the 3D cartesian space relative to the origin of coordinates (i.e., an xyz file). In order to stabilize the calculations and apply the method properly, the molecule has to undergo two transformations: it has to be translated so that its center coincides with the origin of coordinates (0, 0, 0); and it has to be rotated so that its main axis aligns with z, or (0, 0, 1).

The first one is trivial, the centroid of the ring is calculated as the mean of all of the positions of the atoms, and is then subtracted from them.

The second one, the rotation, is not as straightforward. First, the main axis of the molecule has to be calculated. In this case, the main axis is defined as the direction where there is the least amount of variance. Mathematically, it's equal to the eigenvector that corresponds to the smallest eigenvalue of the covariance matrix of the relative coordinates.<sup>4</sup> After having calculated such a vector, it's a matter of calculating the angle that it forms with the z axis using simple dot product, and designing and applying an adequate rotation matrix.

Se10, as well as all of the other sunflowers of the study, only contains heavy atoms that are relevant to the problem, so we can just ignore their chemical elements and treat every point equally. However, it should be noted that in other cases there might be irrelevant atoms such as hydrogens, or parts of the molecule that don't belong to the surface that we are trying to identify. In those situations, special care should be taken: the transformation operations have to be designed around the important atoms, but they should be applied to the whole system.

At this point, the relevant part of the molecule (i.e. the ring object of study), should be centered and aligned with the z axis. All of these preparatory steps ensure the optimal application of the actual method.

2: Such as using interpolation algorithms to calculate the grid points in the empty spaces, or generating compound surfaces by tiling all of the possible planes based on groups of three atoms.

3: The equation of a basic saddle is essentially  $z = x^2 - y^2$ .

**Table 3.3:** xyz coordinates of Se10

x	y	z
0.9154	0.0917	0.0236
-0.0971	0.9542	1.9687
1.0978	0.8552	1.2691
1.8126	1.7897	3.3270
		...

4: That is, the coordinates after having been translated to (0, 0, 0) in the previous step

$$f_i \approx \beta_0 + \beta_1 x_{i1} + \beta_2 x_{i2} + \dots + \beta_p x_{ip} \quad i = 1, \dots, n \quad (3.2)$$

The method itself consists in the optimization of the coefficients of a multiple linear regression model. A linear regression model with  $p$  predictors and  $n$  data points, as shown in Equation 3.2, consists of several elements.  $y$  is the target feature, the one that we wish to predict. The various  $x$  are the predictors, variables on which we base our predictions. The various  $\beta$  values are the coefficients that accompany the predictors and that we want to approximate.

In our case in particular, the bits of real data that we have -our ground truth- are the coordinates of the atoms of the molecule, which include  $x$ ,  $y$  and  $z$  values. Looking at it from the point of view of statistical learning, the problem could be defined as “designing a model that predicts the values of  $z$  by using the values of  $x$  and  $y$ ”. If such a model was developed, we could just input a square grid of  $(x, y)$  values and get the height (or  $z$  value) that they should be placed at to conform to our concept of general surface. There is just a problem with this approach: using just  $x$  and  $y$  by themselves as the predictors is not enough to generate the kind of warped, wavy surfaces that we’re looking for! Just by adding different proportions of  $x$  and  $y$ , the best one could get would be a tilted plane.

That is where the 3D surface selection approach gets mixed in. We can combine the  $x$  and  $y$  values in certain ways in order to generate a wider variety of basic shapes to linearly combine, resulting in a better set of predictors. For this problem, the following set of predictors was chosen:  $x^2$  and  $y^2$  (half cylinders, which result in a saddle when subtracted and a dome when added),  $xy$  (a saddle aligned with the diagonal  $x = y$ ), and  $\sqrt{x^2 + y^2}$  (a cone).<sup>5</sup>

Having defined the elements of the model, it’s a matter of transforming the  $x$  and  $y$  values into their function forms, initializing a linear model, training it with these predictors and the values of the target variable  $z$ , and retrieving the coefficients. This is all done using the convenient scikit-learn,[9] a machine learning framework for the Python language. Without delving deep in how their lineal model’s inner workings, it can be said that it relies on two key parts: a cost function that measures its deviation from the target, and an algorithm that minimizes it by iteratively modifying its coefficients. When the model has been trained, its accuracy is measured by computing the values of the  $R^2$  metric for two sets of points: the original coordinates of the atoms (i.e., the data points that the model is based on), and the middle points of each of the bonds (i.e. a collection of new data that the model hadn’t previously known about).

All of this operations have been combined and encapsulated inside a custom Python command line application available in the author’s GitHub account[10].

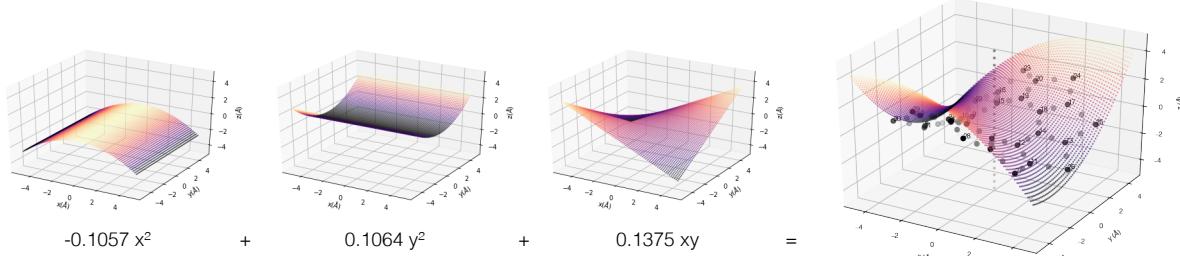
Continuing with the running example, the output of the adjustment of Se10 would be as follows.

```
$ python nics.py surface se10.xyz
```

```
Linear regression results:
x^2: -0.1056911
y^2: 0.1064271
xy: 0.1375246
sqrt(x^2 + y^2): -0.0081293
```

[10]: Iglesias (2020), *nics.py: a command line application to help perform and interpret non planar NICS calculations in Gaussian*

5: It should be noted that this is not proper statistical learning practice: in a real application the predictors shouldn’t have any correlation between them.  
[9]: Pedregosa et al. (2011), ‘Scikit-learn: Machine Learning in Python’



**Figure 3.9:** Linear combination of base 3D functions to model the surface of Se10

R2 score: 0.978916

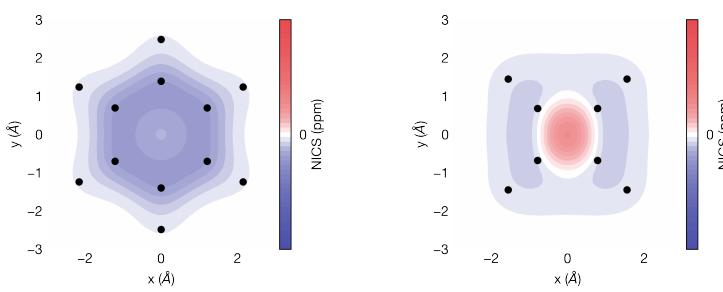
R2 score of atom midpoints: 0.988095

As a way of clearly displaying the result, the idea behind the method, and the elements of the linear combination, the functions have been plotted individually (omitting the last one due to its low contribution) in Figure 3.9.

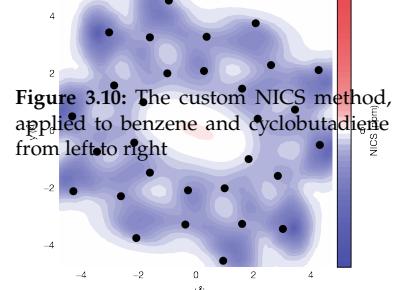
After the surface has been defined, the results of the fitting are used to calculate a square grid of equally spaced points that are all equidistant to this molecule's surface. In this case, a distance of 1 Å is set by general agreement in the literature. Then, both the molecule atoms and the grid points are written into a Gaussian input file (the former as dummy atoms), where the values of NICS will be calculated. The calculation, specifically, estimates the values of the magnetic shielding are calculated with the Gauge-Independent Atomic Orbital (GIAO)[11] method.

When the calculation is finished, the results can be visualized in 3D and plotted using the same program. As for the interpretations of these results, it was said that through this technique aromatic compounds will experience shielding -negative values, marked in blue- on the inside of the ring and deshielding -positive values, marked in red- on the outside. On the other hand, antiaromatic systems will experience the opposite effect. This is the expected behavior and should be the basis for the evaluation of the technique, so to further verify it and illustrate it, the method has been applied to the well known model systems of benzene and cyclobutadiene. Their 2D NICS graphs are included in Figure 3.10.

[11]: Keith et al. (1993), 'Calculation of magnetic response properties using a continuous set of gauge transformations'



The outcome for the Se10 calculation, plotted as a 2D projection onto the  $xy$  plane, is displayed in Figure 3.11. 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



**Figure 3.11:** Custom NICS technique applied to the Se10 system

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. 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.

## 3.6 Spectroscopic characterization

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### Vibrational spectroscopy

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### Raman spectra

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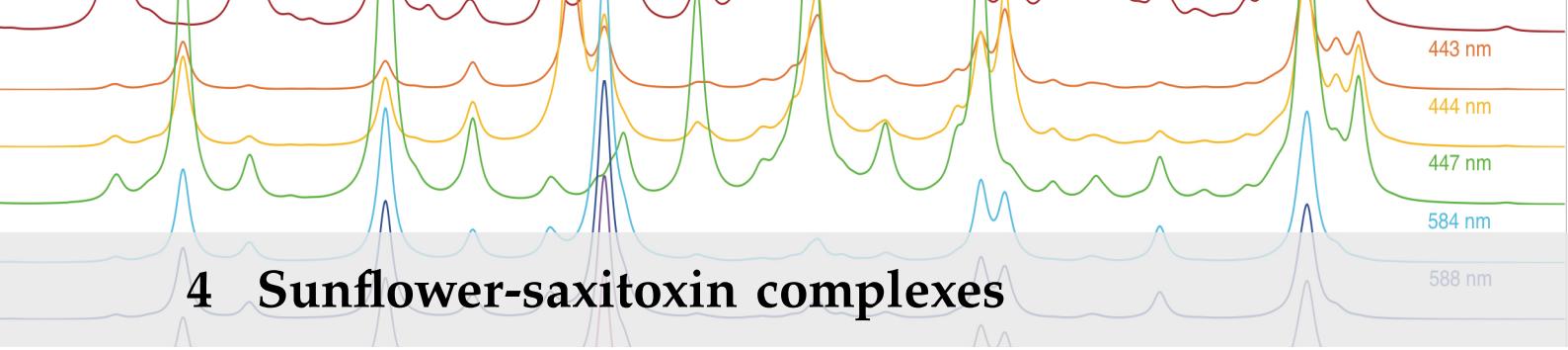
## Electronic spectroscopy

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## UV spectra

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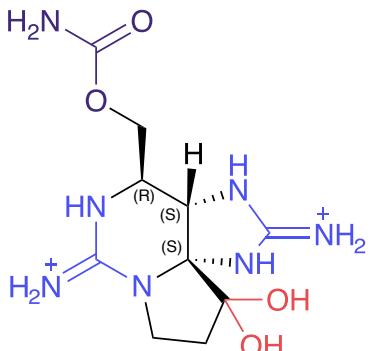


## 4 Sunflower-saxitoxin complexes

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.

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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**Figure 4.1:** Structure of STX

### 4.1 Spectroscopic study of lone STX

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

## 4.2 Study of adsorption

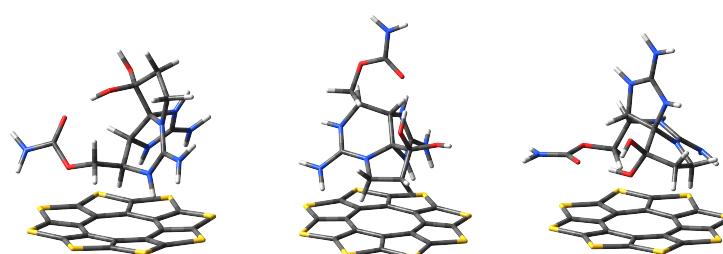
After having characterized the spectroscopic profile of STX, it's time to assess its interactions with the members of the sunflower family, keeping in mind that the main goal of this work is determining if any of them could be a SERS substrate suitable for its detection. The first study that must be carried out, before any spectroscopic technique can be applied, is that of adsorption: how does STX adheres to the flowers, how stable is the resulting complex, what is the nature of that interaction... This is a crucial matter, as there's no point in calculating spectra for a system that isn't stable.

### Sampling and optimization

**Table 4.1:** Relative energies of the STX-S08 conformers, with respect to the most stable one

System ID	Rel. E (kcal mol <sup>-1</sup> )
STX-S08-1	0.000
STX-S08-2	1.337
STX-S08-9	7.133
STX-S08-7	7.504
STX-S08-6	9.896
STX-S08-4	18.554
STX-S08-3	20.321
STX-S08-10	21.734
STX-S08-5	22.529
STX-S08-8	29.715

In order to take into account the possible conformational variability, the STX was manually given an array of different relative positions and angles with respect to the surface of the flowers. Following this idea, 10 different variations were modeled for each of the 18 STX-sunflower pairs, resulting in a total of 180 structures. These various orientations will be referred to as "conformers". All of the conformers for each pairing were optimized at the M06-2X/def2SVP calculation level, and their final energies were compared in order to identify the most stable ones and discard the unstable. Taking the STX-S08 system as an example, the relative energies of all of its generated conformers are displayed in Table 4.1. As it can be seen, the most stable conformer (MSC) is STX-S08-1. However, STX-S08-2, STX-S08-9 and STX-S08-7 are also close energy-wise. A question arises, how can we determine which conformers are stable enough to be important, and which are not?



**Figure 4.2:** Examples of conformers of the STX-S08 system, from left to right, STX-S08-1, STX-S08-9, and STX-S08-3

## Maxwell-Boltzmann statistics

Our answer to this problem consisted in applying Maxwell-Boltzmann statistics to transform these energies into population fractions. This concept essentially translates as the fraction of each conformer that would be present in a macroscopic sample at a certain temperature. As modeled in Equation 4.1,  $p_i$  represents the population fraction of the conformer  $i$ , while  $p_{MSC}$  is the fraction of the MSC of that particular set of conformers. As for the rest of the elements of the equation,  $\varepsilon$  corresponds to the absolute energies of the systems,  $N$  is the total number of conformers in each set (which is 10 in our case),  $k$  is Boltzmann's constant, and  $T$  is the temperature of the system in K (which for the purposes of this study is set at 298 K, or is it 273??).

$$\begin{aligned} \frac{p_i}{p_{MSC}} &= e^{\varepsilon_{MSC} - \varepsilon_i / kT} \\ \sum_{i=1}^N \frac{p_i}{p_{MSC}} &= \frac{\sum_{i=1}^N p_i}{p_{MSC}} = \frac{1}{p_{MSC}} \\ \frac{p_i/p_{MSC}}{1/p_{MSC}} &= \frac{e^{\varepsilon_{MSC} - \varepsilon_i / kT}}{\sum_{i=1}^N \frac{p_i}{p_{MSC}}} = p_i \end{aligned} \quad (4.1)$$

Continuing with the example, the populations for STX-S08 were computed and are displayed in Table 4.2. As an arbitrary threshold, it was decided to filter out all of the conformers with populations lower than 1 %, and to just keep studying the remaining ones. That is, all further calculations that involve the computation of weighted mean values or spectra will only take into account conformers with populations higher than that value.

## Basis Set Superposition Error correction

These optimization calculations have served as a way to estimate the populations of the conformers and to identify the most stable and relevant ones. However, they cannot be used directly to obtain accurate values for the interaction energies due to the Basis Set Superposition Error (BSSE). In this case, this error arises when the STX molecule is close to the sunflower and their basis functions overlap. The part of STX basis functions that comes near the sunflower improves its part of the calculation, and vice versa. This is a problem because in order to get the interaction energy we have to subtract the energy of the complex from the energies of the isolated molecules, but the former has a better calculation level than the latter.

To solve this problem, we used the counterpoise method. For hypothetical molecules A and B, this technique estimates their BSSE by placing the basis functions of molecule A next to molecule B, right where molecule A would go in the optimized geometry of the complex.[12, 13] However, its nuclei are omitted, and just the energy of A is calculated using such an extended basis set. The same process is applied to get the corrected energy of isolated B. Finally, the same formula as in Equation 4.2 is

**Table 4.2:** Maxwell-Boltzmann populations of the STX-S08 conformer set, expressed as percentages

System ID	Population (%)
STX-S08-1	58.56
STX-S08-2	34.16
STX-S08-9	3.30
STX-S08-7	2.83
STX-S08-6	1.08
STX-S08-4	0.03
STX-S08-3	0.02
STX-S08-10	0.01
STX-S08-5	0.01
STX-S08-8	0.00

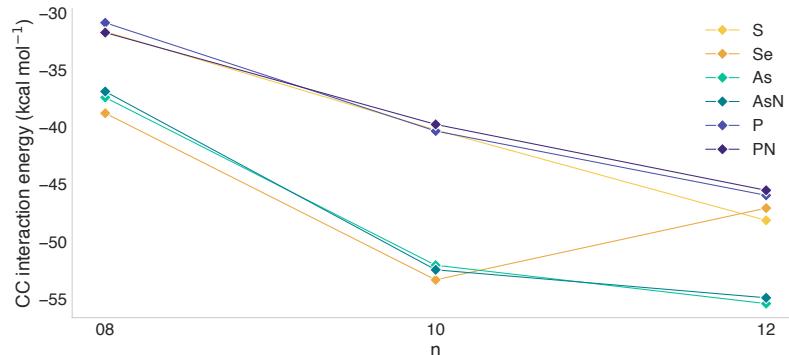
$$V_{STX\text{-}flower} = E_{STX\text{-}flower} - E_{STX} - E_{flower} \quad (4.2)$$

[12]: Duijneveldt et al. (1994), 'State of the Art in Counterpoise Theory'

[13]: Rösch (2003), *Counterpoise Correction*

**Table 4.3:** Maxwell-Boltzmann populations for the 5 most stable conformers in all sets, as percentages, with non significant conformers marked in grey

System n of petals	S %	Se %	As %	AsN %	P %	PN %
08	58.56	79.24	60.96	81.32	40.79	65.13
	34.16	15.57	35.22	15.98	37.48	29.71
	3.30	1.90	2.19	2.16	20.53	4.61
	2.84	1.15	1.38	0.25	0.44	0.24
	1.08	0.14	0.16	0.23	0.32	0.21
10	38.68	61.74	99.64	100.00	86.97	51.05
	36.07	38.26	0.30	0.00	10.12	46.11
	25.21	0.00	0.00	0.00	2.83	2.26
	0.02	0.00	0.00	0.00	0.06	0.56
	0.01	0.00	0.00	0.00	0.02	0.01
12	99.99	58.93	99.75	97.75	93.29	93.83
	0.01	18.98	0.10	2.23	3.26	5.97
	0.00	14.52	0.08	0.01	2.42	0.20
	0.00	6.03	0.04	0.00	0.74	0.00
	0.00	1.55	0.02	0.00	0.16	0.00



**Figure 4.3:** Counterpoise corrected interaction energies as weighted averages for all of the sets

applied to the new values, which results in the counterpoise corrected (CC) interaction energy.

All such energies were calculated for all of the STX-flower system conformers. Their weighted averages using the population values of Table 4.3 were computed, and are displayed in Figure 4.3.

As it can be noted, all of the systems present negative interactions energies, that is, the complex has a lower energy than the sum of the energies of its constituents. This is a good indication that the systems are all stable and can be further studied. All of the families (except for Se) appear to have a common tendency: the higher the amount of petals, the higher the stabilization. This could be due to the flower having a larger area and bending in a way that maximizes the interactions with the STX molecule.

### 4.3 Study of non-covalent interactions

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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.

## 4.4 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

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# 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

