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# Treball Final de Grau

**Designing new tunable materials for organic electronic devices**

**Disseny de nous materials modulables per a dispositius  
electrònics orgànics**

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*Dirac va indicar una vegada que, en principi, la totalitat de la química estava implícita en les lleis de la mecànica quàntica, però que en la pràctica, dificultats matemàtiques prohibitives romanen en el camí...*

Robert S. Mulliken

Primer de tot, voldria agrair al Jordi per tota l'ajuda que m'ha brindat, el temps que m'ha dedicat i pel seu entusiasme, que sempre ajuda a que la feina sigui més agradable.

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**REPORT**





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# 1. SUMMARY

In this work we use computational chemistry to evaluate how an applied electric field can affect the conformation of a  $\pi$ -conjugated linker in 2D materials. To do this we use a model molecular system with different variations on its substituents and evaluate how an electric field can affect the energetic relative stability of their conformations through DFT calculations. Also, it will be explored in these model systems the validity of the first order approximation of the energy of a molecular system with an E-field applied.

These analyses on model systems are done in order to be representative at a small scale of the rotation of a linker in a dimer representation of a 2D-CORF (2D-CORFs are a relative new material). The knowledge acquired on the study of the model system will be used later to analyze the dimer of the 2D-CORF building block which it represents.

It has been found by the model system analysis that as higher is the dipole moment of the molecule is more susceptible to be changed its conformation. On other hand, the results reveal that the first order approximation works better as lower is the polarizability of the substituents, Fluorine is found to be the substituent with less error and because of this, it will be the substituent used in the following step of the study.

Finally, we designed a dimer of a 2D-CORF building block and carried out DFT calculations about the energy related to the rotation of the linker in the singlet and triplet states of the dimer. Moreover, it has been analyzed the strength of the magnetic interactions at all the possible conformations of the linker, related to the calculated energy gap of the multiplicity states. It has been found that the strength of the magnetic interactions changes at different conformations. In addition, has been used the first order approximation to predict the behavior of the dimer in an electric field and it has been targeted the conformation with highest magnetic interactions. Finally, it has been proved that magnetic properties in the material studied can be tuned by an applied electric field.

**Keywords:** computational chemistry, dimer, organic radical, DFT, model system, electric field, magnetism, first order approximation.

## 2. RESUM

En aquest treball, utilitzem la química computacional per avaluar com un camp elèctric pot afectar a la conformació d'un connector pont  $\pi$ -conjugat en materials 2D. Per fer això, utilitzem un model de sistema molecular amb diferents variacions en el seus substituents i s'avaluarà com un camp elèctric pot afectar a l'estabilitat relativa de les seves conformacions a través de càlculs DFT. També, serà explorat en aquest sistema model la validesa de la aproximació de primer ordre de l'energia d'un sistema amb un camp elèctric aplicat.

Aquests anàlisis en els sistemes models seran fets amb la finalitat de ser representatius a petita escala de la rotació d'un connector pont d'un dímer de BB 2D-CORF (els 2D-CORFs són un tipus de material relativament nou). El coneixement adquirit durant l'estudi del sistema model serà utilitzat posteriorment per analitzar el dímer del BB 2D-CORF al que tracta de representar.

En el sistema model s'ha trobat que quant més alt és el moment dipolar de la molècula, és més susceptible a canviar la seva conformació amb un camp elèctric. Per altra banda, els resultats revelen que l'aproximació de primer ordre funciona millor quant més baixa és la polaritzabilitat dels substituents. S'ha trobat que el fluor és el substituent amb un error més baix, i per això, serà el substituent utilitzat per al següent pas de l'estudi.

Finalment, hem dissenyat un dímer del BB 2D-CORF i s'han portat a terme càlculs DFT sobre l'energia relacionada a la rotació del connector pont d'aquest, en els estats singlet i triplet del dímer. A més, s'ha analitzat la força de les interaccions magnètiques en totes les possibles conformacions del connector pont, relacionada amb la diferència energètica entre els estats de multiplicitat. S'ha esbrinat que la força de les interaccions magnètiques varia entre diverses conformacions. A més, s'ha utilitzat l'aproximació de primer ordre per predir el comportament del dímer en un camp elèctric i s'ha pogut controlar el camp elèctric per tal d'estabilitzar la conformació amb les interaccions magnètiques més altes. Finalment, s'ha demostrat que les propietats magnètiques en un material poden ser modulades aplicant un camp elèctric.

**Paraules clau:** química computacional, dímer, radical orgànic, DFT, sistema model, camp elèctric, magnetisme, aproximació de primer ordre.

## 3. INTRODUCTION

### 3.1. PRECEDENTS

Nowadays, many researchers around the world are focused on discovering new materials with interesting properties that provide us a better life. Two dimensional (2D) materials are a huge branch of these, which are extended in a single layer and can be of organic or inorganic composition. In this group of 2D materials can be found well known members like graphene, the first 2D material in the organic field, whose synthesis has opened up very promising opportunities to develop molecular electronics. In the inorganic area molybdenum disulfide ( $\text{MoS}_2$ ) has some interesting electronic properties and luminescence that have led to useful applications [1].

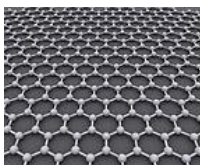


Figure 1. Graphene 2D network.

There are different types of 2D materials whose function depends strongly on their composition and structure. 2D covalent organic frameworks (2D-COFs), are a group of materials that have a characteristic in common: these are organic two-dimensional layers with building blocks (BB) positioned in ordered spacings bonded by linkers. From this definition graphene can be viewed as a 2D-COF where the BBs will be each carbon  $\text{sp}^2$  center, and linkers will be the C-C bonds. However in most 2D-COFs have much more complex structures. This type of structure provides interesting optical and conductivity properties to 2D-COFs. Beyond this general structure, we are particularly interested in 2D-COFs that are important enough to constitute another subgroup inside this: Two-dimensional covalent organic radical frameworks (2D-CORFs). 2D-CORFs are a relatively new materials. The fact that make 2D-CORFs special is that their BBs are organic radicals, namely molecules with a unpaired

electron, which are joined by linkers [2]. 2D-CORFs keep the main essence of all 2D-COFs with respect to their optical and conductivity properties, however, adding the unpaired electrons allows for magnetic properties originating from their localized spins, making 2D-CORFs a class of material with multifunctional properties.

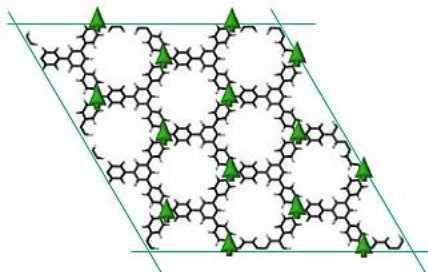


Figure 2. Extended 2D-CORF network.

One condition about radicals included in 2D-CORFs, is their high stability, otherwise such radicals will react, yielding a different material. A well-established class of stable organic radicals are triarylmethyls (TAMs) [3-5], whose structure is based on a central carbon, namely  $\alpha\text{C}$ , where stays the unpaired electron, bonded to three aryl rings. We refer to the plane conformed by the  $\alpha\text{C}$  and the three carbons bonded to it the  $\alpha\text{C}$  plane. The stability of TAMs resides on two facts: on the one hand, the three aryl rings provides steric hindrance that shields the unpaired electron from many reactions, and on the other hand there is a high  $\pi$ -conjugation extended over all the TAM, that allows to the unpaired electron delocalize to the *ortho*- and *para*- positions of each aryl ring, decreasing the energy of the system and stabilizing the molecule.

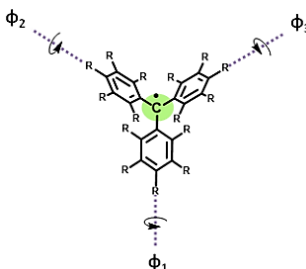


Figure 3. TAM general structure.

These organic radicals have the potential to give unique physical properties, like conductivity, magnetism and optical, that could lead to useful applications in transistors,



spintronics and non-linear optics. On the other hand, there are many types of linkers that can bond the TAM radicals, and depending on which is chosen, the 2D-CORF properties are different. A really interesting property of these linkers, is that they can contain fragments that can be rotated by means of an external electric field (E-field), changing in this way the electronic structure of the 2D-CORFs.

In 2D-CORFs, the properties like conductivity and magnetism, are given by the electronic structure. Joining this fact and the previous idea of the possible rotation of the linkers by an E-field, this means that by applying an E-field it could be possible to modify the 2D-CORF properties, thus making a material with tunable properties. This fact provides 2D-CORFs (such as COFs) an extended range of possibilities depending on the chemical structure, opening up the possibility to synthesise new 2D materials with programmed properties.

### 3.2. TUNABLE PROPERTIES

Properties are one of the main reasons that make materials different between them, so the capacity to tune these attributes would be a significant advantage of a material. Frontier orbitals and overlap of molecular orbitals play a key role in defining the properties of a chemical system. As it has been mentioned in section 3.1., 2D-COF materials potentially have a very interesting electronic structures that are key to their material properties. 2D-CORFs are particularly interesting due the electronic structure of a  $\pi$ -conjugated system providing the conductive pathways, and radicals providing the magnetic connection between spins. There are different ways to change electronic structure in order to tune 2D-CORFs properties, for example: mechanical forces [2], temperature and E-field [6]. These external variables, acts in different ways to produce their effects.

There are a variety of possibilities to apply a mechanical force to a molecule, for example: tensile strain and compression. When a tensile strain is applied and material is stretched, what happens at the microscale is that bond lengths gets longer, some angles twist and other conformations become favorable. As a consequence, these events induce an increase of the 2D-COFs cell parameters, directly related to different properties such as magnetism, conductivity and spin localization [2, 7-9].

In other way, temperature effects the macrostate of the system. At the quantum scale, where temperature hasn't sense (because it is a magnitude directly related to the macroscopic

average kinetic energy of a system), the concept of microstate becomes more logical. A microstate is one possibility of all the possible states of the system, for example: in a 2D-CORF case, the rotation angle of the linker could have a value between 0 and 360 degrees. This is useful in microscopic world where there are only a few linkers, but not in macroscopic world, where the magnitude order of linkers of a system is close to Avogadro's number ( $\approx 10^{23}$ ), and defining the microstate of a system isn't practical as each angle of each linker should be defined. Statistical mechanics is the tool that allows to apply thermodynamics (including temperature) to a large system, like a 2D-CORF, giving information of the probability of the linker to be at one rotation angle on another, constituting the Boltzmann population, and giving rise to the macrostate of the system. Depending on the type of system we are working on, different formulas need to be applied. The system of interest of this study will be part of the canonical ensemble and these are the formulas that need to be applied in order to describe the macrostate of the system.

$$Z = \sum_{i=1}^n e^{\frac{-E_i}{kBT}}$$

Equation 1. Partition function expression of the canonical ensemble.

$$p_i = \frac{e^{\frac{-E_i}{kBT}}}{Z}$$

Equation 2. Probability of a substructure of a system to be in a certain microstate.

being  $Z$  the partition function,  $n$  all possible microstates,  $E_i$  the energy of the microstate,  $kB$  the Boltzmann constant,  $T$  the temperature and  $p_i$  the probability to find the microstate with  $E_i$  energy.

As it's shown in Equation 2, temperature plays a huge role in defining a macrostate, so it's change results in a different macrostate, changing the rotation angle populations of many linkers, and consequently changing the electronic structure of the 2D-CORF, and finally switching the macroscopic properties related to this electronic structure [5].

Finally, when an E-field is interacting with a molecule, the energy of this molecule changes in a certain way that can be explained by the following a Taylor series [10]:

$$E = \sum_{i=1}^{\infty} -\frac{F^i}{i!} \alpha_i = E^0 - \mu F - \frac{1}{2} \alpha F^2 - \frac{1}{6} \beta F^3 - \dots$$

Equation 3. Energy of a system with an electric field applied and a Taylor expansion including the zero, first, second and third terms.

being  $E$  the energy of the molecule in the electric field,  $E^0$  the energy without electric field,  $F$  the value of the electric field, and  $\mu$ ,  $\alpha$ ,  $\beta$  are the components of dipole moment, polarizability and the first hyperpolarizability, respectively [10]. This energy change of the molecule, in our case a 2D-CORF, makes that other conformations could become more energetically stable, inducing a change of the conformation of the molecule. As it's shown on the Equation 3, the parameters of a molecule that allows this energy switch are the dipole moment, polarizability and first hyperpolarizability, in decreasing order of importance in small  $E$ -fields. This information means that if the linker of a 2D-CORF has an inherent dipole moment, the linker conformation would be the unique part of the material that could change, because the organic radicals are confined to be in the 2D plane.

A consequence of these facts is that when an  $E$ -field is interacting with a 2D-CORF, it can induce a conformational change of an appropriately designed linker, which can then modify the electronic structure and as well the related properties related. [6].

### 3.3. PROJECT STUDY

In this work, will be studied through Density Functional Theory (DFT) calculations a dimer of a BB of a 2D-CORF, whose linker can rotate by means of an external  $E$ -field, providing a way to tune the 2D-CORF properties. This study will thus use a finite molecular model to be representative of an extended 2D-CORF network.

However, a previous work needs to be done with a smaller model system, in order to firmly understand the behavior of the linker rotation upon application of different  $E$ -fields. This model system will have 3 different variations of the substituents that mainly provides the dipole moment, in order to compare them and chose the better one to include on the linker of the 2D-CORF BB.

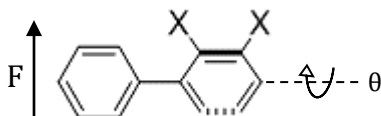


Figure 4. Structure of the model system with the direction of  $E$ -field that will be applied.

In this section, also will be investigated the range of validity of a first order approximation of equation 3, in order to determine its possible use with some of the BBs of the 2D-CORF calculations.

$$E = E^0 - \vec{\mu} \cdot \vec{F}$$

Equation 4. First order approximation of Equation 3.

Once this is done, the dimer of the 2D-CORF BB will be studied, using all the knowledge learned by studying the model systems. This 2D-CORF need to satisfy three conditions in order to be a good candidate for having tunable properties: the BB radical has to be stable, the main dipole moment of the 2D-CORF has to be provided by the linker, and different rotation angles of the linker have to be related with a different conjugations of the 2D-CORF. In this study, the BB will be a TAM where aryl rings will be six-membered aromatic rings with two chlorines in positions *ortho*- respect to the carbon bonded to the  $\alpha$ C, serving one of the three conditions. This specific TAM is especially stable, due the chlorines that increase the steric hindrance to make the central unpaired electron more inaccessible. The linker chosen for this study is an aromatic ring of six members, with two triple bonds in *para*- positions that joins the TAM with the linker aryl ring. Also, the two substituents that provides the dipole moment of the 2D-CORF are bonded in positions 2 and 3 of the aromatic ring. This linker structure, accomplished the two remaining conditions, one the one hand the dipole moment is rightly inserted, and on the other hand the aromatic nature of the linker will affect the  $\pi$ -conjugation of the material, creating pathways between BBs when it is in the right angle respect to the  $\alpha$ C plane.

After the BB and the linker presentations, some calculations will be done in order determine the strength of the E-field that leads to the linker rotation, and also an analysis of the effect of temperature using statistical mechanics will be carry out to determine the populations of rotational angles of the linker at several temperatures. All these calculations about the dimer of the 2D-CORF building block will be done in a way to be representative of a 2D-CORF. Finally, will carry out a quantitative analysis of the magnetic property changes induced by the conformational rotation of the linker due to the E-field.

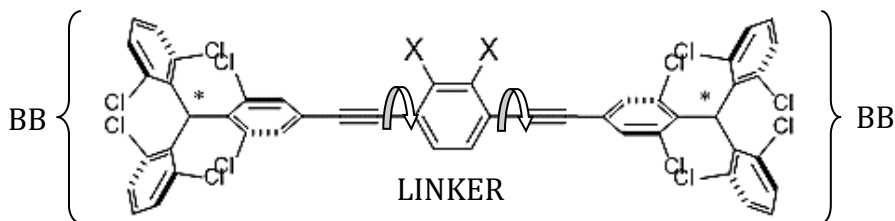


Figure 5. Structure of the dimer of the BB 2D-CORF.

## 4. OBJECTIVES

The scope of this project is:

- a) To determine the range of validity of the first order approximation (see Equation 4) with the strength of E-field applied.
- b) To analyze the intensity of an E-field needed to induce a conformational change.
- c) To determine the population of linker angles at given conditions of E-field and temperature.
- d) To analyze how changes in the linker conformation affect the strength of the magnetic interactions in the dimer of the 2D-CORF.

## 5. COMPUTATIONAL DETAILS

### 5.1. DENSITY FUNCTIONAL THEORY APPROACH

Density Functional Theory (DFT) is a first principles computational quantum mechanical modelling used for solving the Schrödinger Equation of polyelectronic systems through certain approximations. In this way, the electronic structure and properties of a system can be determined. The foundations of DFT were reported in in two papers published in the 60's: Hohenberg-Kohn in 1964 and Kohn-Sham in 1965 [11-12].

DFT is based on solving the electronic density using a functional of a system instead of solving the Schrödinger Equation through the variational method as do *ab initio* calculations. The advantage of DFT method is that reduces the degrees of freedom to three, allowing one to do calculations of large systems and doing calculations faster.

### 5.2. STUDIED CONDITIONS

The calculations of the model system, for all the substitutions studied, will use the same protocol. Each model will be studied the conformations resulting by twisting the angle of the

linker between the aryl rings from  $10^\circ$  to  $170^\circ$  in steps of  $5^\circ$ . These conformations will be named as the standard scanning of the molecule.

After the standard scanning at zero-field, the standard scanning at different intensities of E-field will be calculated, from 0.001 a.u. to 0.015 a.u. in steps of 0.002 a.u. and an extra higher E-field will be applied in order to analyze an extreme case, 0.03 a.u. (where a.u. is atomic units, equivalent to  $5.14 \times 10^9$  V/cm). These ranges of E-field have been found to be reasonable for this type of calculation [6].

For the calculations of the BB dimer of the 2D-CORF, due to the nature of the molecule, instead of using the standard scanning, we will scan from  $0^\circ$  to  $360^\circ$  in steps of  $15^\circ$ . From our study of the model system the intensities of the E-field were chosen to be from 0.001 a.u. to 0.007 a.u. in steps of 0.002 a.u.

All the DFT calculations provide information about the energy of the system and its dipole moment, the two main characteristics needed in this study.

### 5.3. METHODS

In order to do the DFT calculations, the z-matrix of the system must be defined (see z-matrix example Appendix 1) and must be set up for each type of calculation. In Table 1 we summarize all the parameters used in the DFT calculations (see input example on Appendix 2), by using Gaussian09[13].

CONDITION	CALCULATION VALUE
Type of calculation	z-matrix optimization
Max. number of steps (MaxStep)	5 to 15
Max. number of SCF cycles (MaxCycles)	200
Functional	PBE0
Basis set	6-31+g (d)
Field (10000×a.u.)	X+10 to 300
SCF Convergence criterion	Tight

Table1. Values of the most important parameters of the DFT calculations.

## 6. RESULTS AND DISCUSSION

In this section, all the results related to the DFT calculations are shown, with their consequent discussion. The description of the results and discussion is organized in two main sections: calculations about the model system and calculations about the dimer of the 2D-CORF BB studied.

The part of the model system will contain the three substitution variations, one for each substituent: fluorine, cyano and bromo. Inside these sections, for each substituent, will be shown various aspects, being the first the behavior of the molecule at zero field and with an E-field applied. The next facet to comment will be how good is the first order approximation (see Equation 4) by correcting the contribution of the energy of a molecule in the presence of an E-field. Also it will be shown and discussed the Boltzmann populations of the molecules at the different temperatures for each E-field applied, and how are affected if they are calculated through the first order energy correction of the molecule with the E-field applied (see Equation 4). In addition, a comparison of results for different systems will be shown.

The block of the dimer 2D-CORF BB will contain also various aspects. First one will be the behavior of the dimer without an E-field for the singlet and triplet state. The following aspect will be the prediction of the behavior of the dimer ground state when the first order E-field energy correction approximation (see Equation 4) is used. This is why the previous work with the model system is so important, because if the first order approximation works well, a lot of heavy DFT calculations would not be necessary, because they can be predicted by simply adding the energy contribution due to the E-field by using the first order approximation. We will also explore the temperature dependence on the conformation of the linker. This will be done by analyzing the Boltzmann populations at different temperatures at zero field, and in each field calculated through the predictions using the first order approximation. We will also explore the dependence on the conformation of the linker of the magnetic interactions. In order to do this, the energy gap between the singlet ground state and the triplet ground state will be calculated. The energy difference between these two states is proportional to the strength of magnetic interactions between the BBs in the CORF dimer.

## 6.1. DIFLUORO-SUBSTITUTED MODEL SYSTEM

As mentioned earlier in section 6, the difluoro-substituted model system (see Figure 4) will be the first substitution explored. These are the first substitution calculations in order to explore first the simplest case. This is the simplest substitution for this study because fluorine it's the most electronegative atom, a property that creates a high dipole moment. If dipole moment is high, the first term of the correction ( $-\mu F$ , see Equation 3) becomes more important than the others. Because of this, it's more possible that the first order approximation works better. Also, fluorine it's a small atom, and it helps to simplify the problem in different ways. This small size, it's directly related to a low polarizability, reducing more the second term of the correction ( $-\frac{1}{2}\alpha F^2$ , see Equation 3) and decreasing its importance to the correction, in order to make the first order approximation more viable. Another effect of this smaller size is that it reduces the steric hindrance between the fluorine atoms and the hydrogen atoms of the other ring in a coplanar conformation. This fact simplifies the problem in order that the other variables that could affect the conformation of the molecule are reduced, becoming a purer problem in taking as the principle mechanism of rotation the interaction between the E-field and the dipole moment. Also, this first case is simplified in other way, with respect to the E-field applied. This E-field could be applied in different intensities, but as it's a vector, it could be applied in different directions. In this case we will only explore the effect of the E-field in one direction, which is parallel to the two rings when they are in a coplanar conformation, perpendicular to the bond that joins the two aromatic systems and pointing to the side of the two fluorine atoms.

### 6.1.1. ZERO-FIELD AND E-FIELD APPLIED ANALYSIS

In the model system with two fluorine atoms, the 2,3-difluorobiphenyl, has been found that in the scanning of the rotation angle between aryl rings at zero field contains two energy minima, approximately at the same relative energy value. As lower is the energy, more stable is the conformation angle, so the minima describe the most stable angles, located in this curve at  $45^\circ$  and  $135^\circ$  (see zero field curve, on Figure 6). In addition, the energy curve of 2,3-difluorobiphenyl presents maximums at  $10^\circ$ ,  $90^\circ$  and  $170^\circ$ . Related to the previous explanation of the meaning of the energy, it means that these maxima represent the most unstable angular conformation. The highest of these maxima are at similar energies and correspond to the  $10^\circ$  and  $170^\circ$  angles, while the one corresponding to  $90^\circ$  is lower in energy.



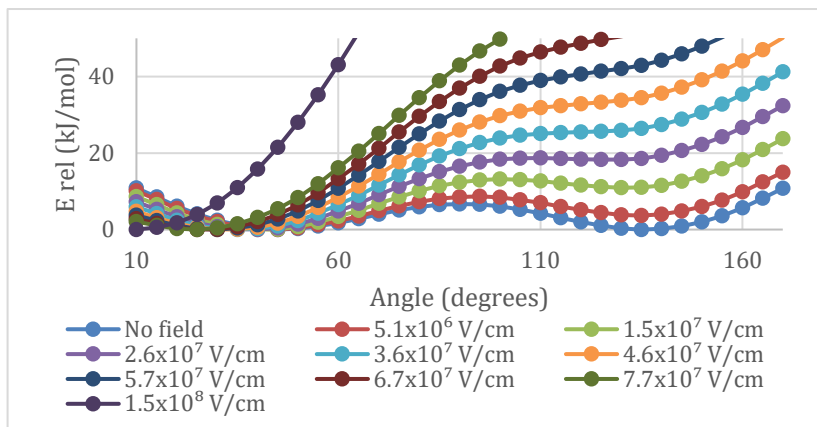


Figure 6. Zero-field and energy curves at different E-fields of difluoro-substituted model system.

These energy minima and maxima can be explained by an interplay between  $\pi$ -conjugation and steric hindrance. The model system used in this study has two  $\pi$ -systems, each one in each aromatic ring. What  $\pi$ -conjugation does, is to delocalize the electrons of the  $\pi$ -systems, distributing the negative charge in more space and thus corresponding to different resonant structures. As a result of this, the energy of the  $\pi$ -system decreases, increasing the stability of the system (see Figure 6). This gain of stability is proportionally related to the space where electrons are delocalized, so when a  $\pi$ -conjugation is more extended, it is lower in energy. In this model system, if the two  $\pi$ -systems were overlapping, it will result into one  $\pi$ -system extended over all the molecule. In this way, the space for electron delocalizing increases and then the conformation becomes more stable. It's important to know that the  $\pi$ -systems are overlapping when they are near to one another and are in the same plane. In this model system, it's easy to notice that the two  $\pi$ -systems are close, so they are only separated by one bond, so the condition for the extended  $\pi$ -conjugation it's that the two  $\pi$ -systems must be in the same plane. This happens when the two aromatic rings are in the same plane, because the  $\pi$ -systems are perpendicular to this. So, in conclusion, there will be an extended  $\pi$ -conjugation when the angle between the two rings are  $0^\circ$  or  $180^\circ$ . Besides, the overlapping percentage of the  $\pi$ -systems it's reduced as the angle increases, becoming gradually more unstable conformations between  $0^\circ$  and  $180^\circ$ , being  $90^\circ$  the more unstable due to the two  $\pi$ -systems are completely perpendicular and there isn't any  $\pi$  overlapping.

The other factor that could affect to the energy curve will be the steric hindrance, that is basically is manifested when atoms are too close. Because of this proximity, there is a repulsion between the electric charges of the electrons, fact that make this an unstable scenario (see Figure 6). In the model system studied, the steric hindrance increases as the aryl rings becomes coplanar, because fluorine and the respectively hydrogen atomic of the other ring are getting closer. One the one hand, steric hindrance becomes minimum when the pair of atoms, hydrogen-fluorine, at are the maximum distance at  $90^\circ$  and, on the other hand, steric hindrance becomes a maximum when the angle between the aromatic rings are  $0^\circ$  and  $180^\circ$ .

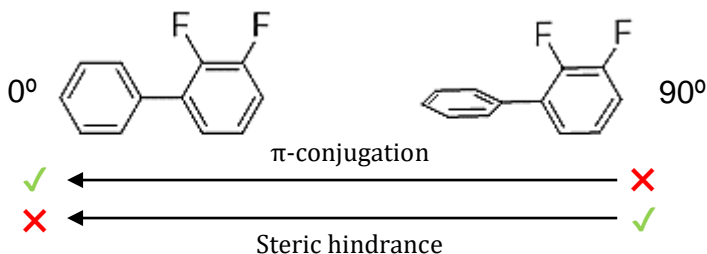


Figure 7. Interplay between  $\pi$ -conjugation and steric hindrance.

After the explanation of these two concepts ( $\pi$ -conjugation and steric hindrance) the interpretation of the energy curve at zero field becomes easier to understand. When the angle between rings is  $10^\circ$ , there is an intensification of the steric hindrance, creating an unfavorable conformation, which gives rise to a maximum that appears on the energy curve. On the other side of the graphic, at  $170^\circ$ , we have the same situation and the arguments are the same as at  $0^\circ$ . These similarities are because of the symmetry of the molecule, replicating the same interactions when the fluorine atom gets closer to the other ring from one side and the other side. The last maximum is located at  $90^\circ$ , angle where  $\pi$ -conjugation it's totally disabled, becoming energetically unfavorable. Finally, the maxima due to the steric hindrance ( $10^\circ$  and  $170^\circ$ ) are higher than that provided by the  $\pi$ -conjugation, noticing that a high steric hindrance is slightly more unfavorable than absence of  $\pi$ -conjugation. Between these extremes scenarios, there are intermediate situations with respect to the two factors, finding the equilibrium at  $45^\circ$  and its symmetrical angle at  $135^\circ$ , where we have the ideal mix of a relevant percentage of  $\pi$ -system overlapping and a small steric hindrance.

Related to the energy curves of the molecule with E-field applied, it can be seen that these are quite different comparing with the zero-field curve (see Figure 6), differing more as the

strength of the E-field increases. The more stable angle changes in each intensity of E-field, showing a trend to be more shifted to a coplanar structure as higher is the E-field, through reducing the value of the most stable angle.

These energy curves can be explained with the previous concepts of  $\pi$ -conjugation and steric hindrance, but must be added another important variable, the E-field. In a simplified situation, where polarizability and the chemical nature of the system can be negligible, the E-field only interacts with the dipole moment of a system. The energy of the system provided this interaction follows the next equation:

$$U = -\vec{\mu} \cdot \vec{F}$$

Equation 5. Potential energy of a dipole in a homogeneous electric field.

being  $U$  the potential energy of a dipole,  $\vec{\mu}$  the dipole moment and  $\vec{F}$  the E-field. One of the interesting points of Equation 5, it's to analyze when the potential energy becomes minimised at given values of the of dipole moment and perfectly defined E-field. This is interesting because at minimum energy, the system becomes energetically favorable and stable, and the system will tend to this situation. Analyzing the scalar product in Equation 5, can be noticed that the minimum value of potential energy is reached when the vectors of dipole moment and E-field have the same direction and sense. Because of this, can be concluded that the trend of a pure dipole is to align its dipole moment with the E-field. It should be remembered that in chemistry, the direction of the dipole moment it's defined from positive to negative charge, in this way more or less pointing in an intermediate region between the two fluorine atoms. This alignment is complete when the angle between the dipole moment vector and the E-field vector is  $0^\circ$  and totally misaligned at  $180^\circ$ , resting to other angles in intermediate situations. This trend of the alignment will be stronger when the dipole moment or/and the E-field increases in module, because this makes the scalar product higher, reducing the potential energy and providing a more stable state.

Now, the energy curves of the molecule can be explained by an interplay between three factors which can be compared with the zero-field curve:  $\pi$ -conjugation, steric hindrance and the E-field (considering its magnitude, direction and sense). Can be seen that one of the main differences of the field curves is that the minimum at  $45^\circ$  is shifted to lower angles when the intensity of the E-field increases, in a proportional way. This is because as higher is the E-field, the trend of the dipole to align with the E-field increase, allowing the molecule to overcome the

steric hindrance present at that angle. It's convenient for this to remember in which direction and sense is the E-field applied (see Figure 4), figuring out that the angle with better alignment would be  $0^\circ$ .

Also, can be seen that as the intensity of the E-field increases, the symmetrical minimum of  $45^\circ$  at  $135^\circ$  it's disappearing, being indistinguishable at E-fields higher than  $2.6 \times 10^7$  V/cm. This is because the influence of the E-field breaks the symmetry of the system. The presence of this E-field provides different energies to symmetric angles because the dipole moment vectors of these angles point in different directions with respect the vector of the E-field. In this case can be deduced that, due to the nature of the study, the angle between the dipole moment vector and the E-field vector is the same as the rotation angle of the conformation. By knowing this, is easier to see that at the conformation of  $135^\circ$  the two vectors of interest are very misaligned, and as the strength of the E-field increases, this conformation will be more unstable. This argument can be used to understand why all the plotted angles bigger than the stable angle of  $45^\circ$  at zero field curve becomes more unstable. This is because as higher is the field their misalignment of the dipole moment respect to the field is more noticeable and their energy is increased, reaching always the maximum at  $170^\circ$  where there are the biggest misalignment and high steric hindrance. On the other side, all the plotted angles smaller than the stable angle of  $45^\circ$  at zero field curve become more stable. This is because as higher is the E-field their alignment of the dipole moment respect to the E-field is more noticeable, being able to get over the steric hindrance. Another consequence of this fact, is that the minima created by the E-field are deeper as stronger is this E-field, constituting a more stable relatives minima by increasing the intensity of the E-field.

On the extreme case calculated of the E-field of  $1.5 \times 10^8$  V/cm applied, its energy curve follows the trend provided by the previous curves at smaller E-fields, shifting the minimum towards coplanarity, overcoming a really high steric hindrance.

### 6.1.2. E-FIELD APPLIED CORRECTIONS ANALYSIS

Related to the energy corrections using the first order approximation (Equation 4) on the curves with E-field applied, can be calculated the zero-field curve based on each curve with an E-field applied. This calculation of the zero-field curve can be done by correcting each energy angle with an E-field applied by using the Equation 3, but as an objective is to determine the range of validity of the first order approximation (see Equation 4) with the strength of applied

field, it will be done by using the first order approximation. This is a simple calculation that is done by adding to the energy with an E-field applied the scalar product of the dipole moment at the right angle with the E-field. If the first order approximation would be perfectly valid, subtracting the first order dipolar energy correction (see Equation 4) from each point of the energy curves in Figure 6 would result in all curves being reduced to the zero-field curve. As we can see on Figure 7 this doesn't happen, meaning that the first order dipolar energy correction isn't perfectly valid, even though it can be understood through the Equation 3. What it's happening is that polarizability and first hyperpolarizability aren't zero (or maybe, based on the mathematics, only one of this is zero), and these contributions should be added if we are searching for the perfection in this calculation. However, although the first order correction isn't exact, clearly can provide the main characteristics of the zero-field curve (see Figure 8). Nevertheless, as can be seen in Figure 8, that the quality of this correction varies with the intensity of the E-field applied, being more effective at small values of E-field where second and third term of Equation 3 are small, until being completely useless at the curve based on the curve calculated with  $1.5 \times 10^8$  V/cm of E-field applied.

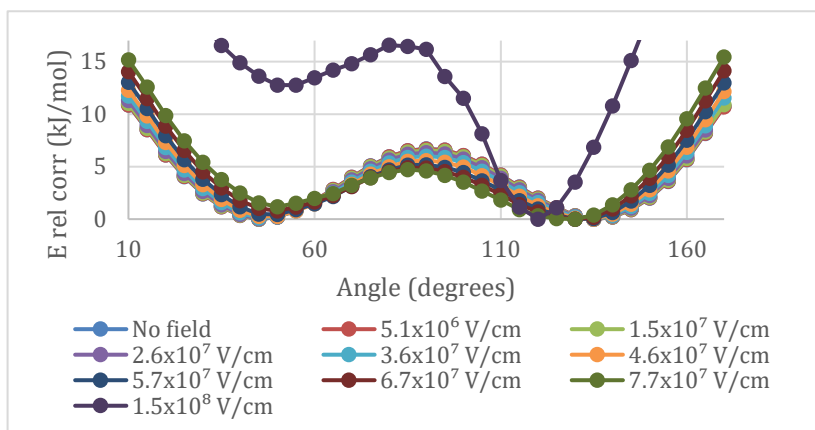


Figure 8. Zero-field and the energy curves corrected by first order approximation.

In order to analyze better the error of this correction has been plotted the difference in each angle between the zero-field curves calculated based on the curves with E-field applied and the zero-field curve (see Figure 9). If the first order approximation would be perfectly valid, these curves of this plot would result in a straight line at zero.

Now, paying attention to Figure 9, can be seen that the energy error correction increases as the intensity of the E-field increases. This fact could be expected because as we can see on Equation 3, the second and third term increases and gets more importance, reducing its negligibility.

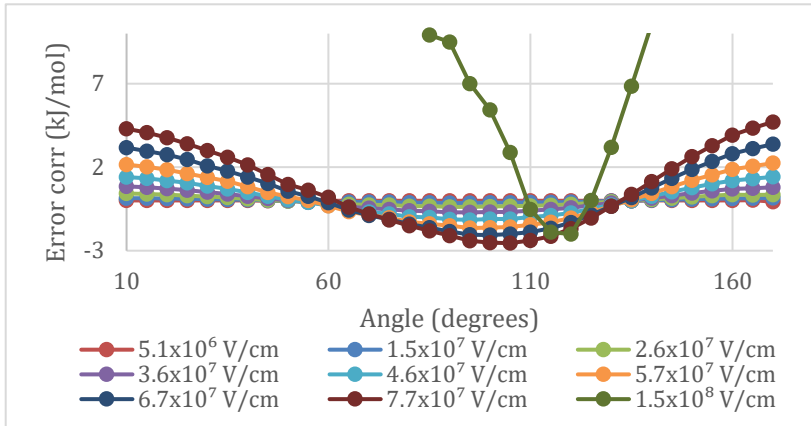


Figure 9. Error by using the first order approximation.

Besides, can be noticed that the error of the first order correction is higher at the maxima of the zero-field curve, and this is reducing while is getting closer to the inflection points, being more precise at the first of these. Also, because of the dependence of the error with the E-field, can be seen that the curve based on extreme case of E-field it's totally different, demonstrating the low validity of the first order approximation at these ranges of E-field.

### 6.1.3. BOLTZMANN POPULATIONS ANALYSIS

Related to the Boltzmann populations at different temperatures, can be observed in Figure 10 that temperature plays a key role on determining which angles are more populated. These has been calculated by a program (using Fortran90 as a programming language, see Appendix 3) that has been done for this specific part of the study, based basically on Equations 1 and 2. At low temperatures, the most populated angles with a high selectivity are those which correspond to the minimum energy angle. Then, as temperature increases this selectivity is getting worse by following the Equation 2, allowing the population of more angles close to the minima angles of energy, angles that are in an intermediate stability.

When temperature isn't a relevant factor, at 1 K, there isn't enough thermal energy to populate angles that are not a minimum, so the selectivity of the populated angles is very high

over these minima. Besides, the most stable minimum receives a more probability to be populated (see Equation 2) because it is lower in energy.

As mentioned earlier, when temperature increases this selectivity it's getting worse, changing the probability to find the minimum angle of  $45^\circ$  and  $135^\circ$  from 60% and 40% to 10% and 10% respectively, at temperatures near (301 K) to room temperature (298 K). This loss of selectivity at zero-field it's expected, so all conformations are relatively near in terms of energy, these being more accessible. Also, it must be pointed out that at every temperature, the most populated angles are always the most stable.

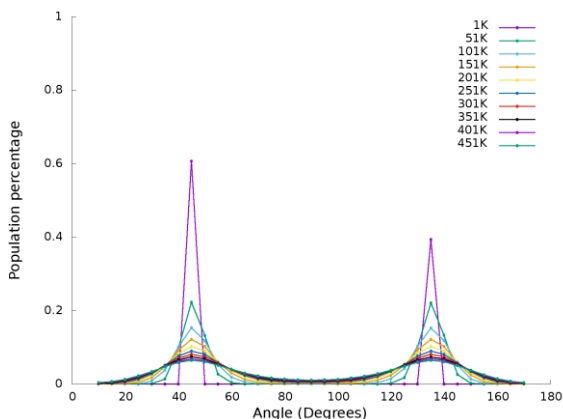


Figure 10. Probabilities to find a certain angle at a certain temperature at zero-field.

Now, when we explore the dependence of these Boltzmann populations with the E-field applied (see Figure 11), we can see the E-field has a key role. In this analysis only will be plotted two interesting temperatures: 81K (near to nitrogen liquid temperature) and 301 K (near to room temperature). In each E-field applied, the most populated conformation is shifted, matching to the trend of the minima on the energy curves. As have been seen before, at the zero-field Boltzmann populations, in each temperature always the most populated angle is the most stable.

In addition, at any E-field the loss of the stability conformation at  $135^\circ$  due to the breaking of the symmetry it's shown by very small probabilities to be found this  $135^\circ$  angle, near to 0%. Also, another coherent trend respect to the energy curves, is that as the E-field increases, the deeper is the minimum, and the more stable is the respective conformation, and, as a result, the probability to find the conformation is higher.

One interesting characteristic is that at zero-field applied, the selectivity of the maximum angle at room temperature is 10% while with an E-field this is improved to 20% and reaching the 40% in the extreme case of the highest E-field.

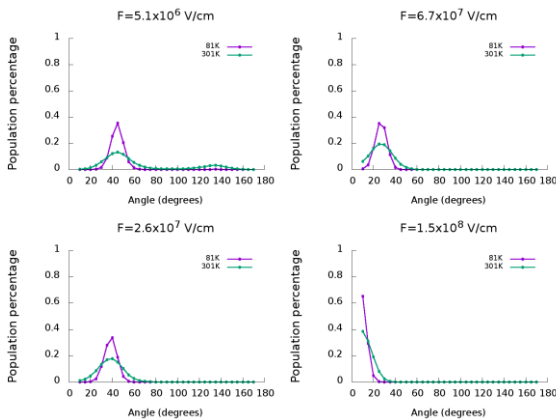


Figure 11. Probabilities to find a certain angle at a certain temperature with different E-fields.

Another coherent issue is that at liquid nitrogen temperature, the selectivity of the most stable conformation it's better due to the low thermal energy, although not enough to increase more the conformation of the nearby angles.

### 6.1.4. BOLTZMANN POPULATIONS CORRECTIONS ANALYSIS

Now, has been calculated the Boltzmann populations based on the curves calculated by using the first order approximation to the calculations with E-field (see Figure 12). If the first approximation correction is totally valid, the Boltzmann populations would be the same as those a zero-field, but previously it has been found that this correction isn't exact.

When the E-field applied is the smallest calculated, the correction matches better with the Boltzmann populations at zero-field. Other graphs are more distinct from the zero-field graph because to the error correction is higher. Also, can be seen that an important error is that the most populated angle is clearly shifted to 135°. This is, because of the corrections at higher E-field, this conformation is relatively more stable than that at 45°. In conclusion, when the corrections favor the stability of a conformation respect to its symmetry, there is a high error, concluding that the first order approximation in this ranges of E-field doesn't work in order to calculate the Boltzmann populations, but it gives the correct information by interpreting through the symmetry of the system.



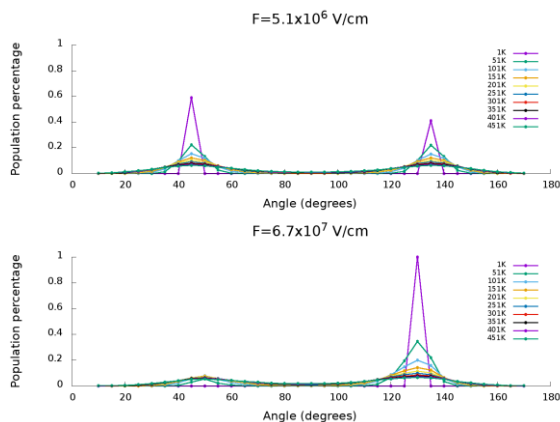


Figure 12. Probabilities to find a certain angle at a certain temperature based on the corrections of the first order dipolar contribution.

## 6.2. DINITRILE-SUBSTITUTED MODEL SYSTEM

In this section the calculation results of the model system dinitrile-substituted will be described and compared with those done on the difluoro-substituted system. The main difference between fluorine and cyano is their size. Because of this, it's a reasonable prediction that the behavior of the model system will be approximately the same, but steric hindrance could take a more important role. In order to compare better this variation, the E-field will be the same in intensity and direction. (see Figure 4)

### 6.2.1. ZERO-FIELD AND E-FIELD APPLIED ANALYSIS

In the model system with two cyano substituents, 2,3-dicarbonitrilebiphenyl at zero-field, has been found (see Figure 13) that the more stable angles of its conformation are 50° and approximately its symmetrical case of 125° in this case (the perfect symmetry would be 130°, but this is slightly broken because has been proved on the output calculations that one of the two rings isn't completely planar). Also, the energy curve of the rotation angle presents three maxima, one at 90° when the two rings are perpendicular, and at 10° and its symmetrical 170°. The maximum at 90° is significantly lower than the others.

All these characteristics can be explained using the same concepts as has been described with the model difluoro-substituted system (see section 6.1.), through an interplay between  $\pi$ -conjugation and steric hindrance.

At the maximum localized at 90° happens the same as that on the difluoro-substituted model system, in this conformation  $\pi$ -conjugation is completely disabled, becoming an unstable

conformation relative to the other situations. On the other hand, when steric hindrance is important creating unstable conformations at  $10^\circ$  and  $170^\circ$ , this results in the remaining maxima. The energy difference between the  $90^\circ$  maximum and the higher maximums is bigger than in the difluoro-substituted model system because as cyano is a bigger substituent than fluorine, this causes a higher steric hindrance and disfavors more these specific conformations. Another consequence of this fact, is that the minima are deeper, being more stable relatively which possibly will be reflected in a higher Boltzmann population.

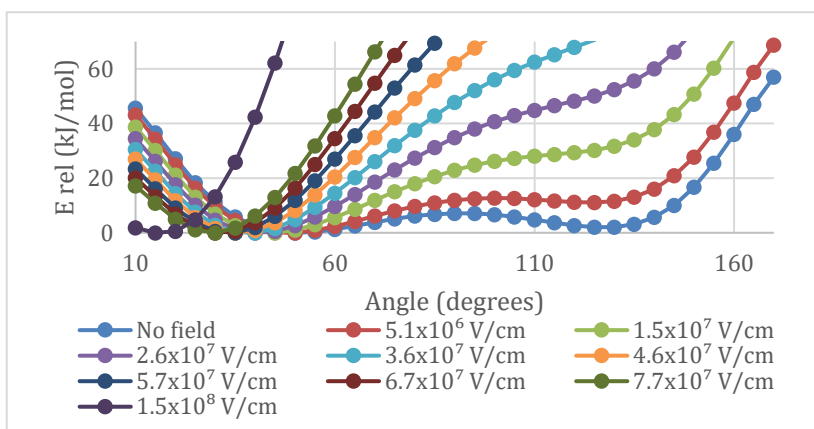


Figure 13. Zero-field and energy curves at different E-fields of dinitrile-substituted model system.

Paying attention to these minimums, the equilibrium mixture of steric hindrance and  $\pi$ -conjugation, are closer to  $90^\circ$  than in the difluoro-substituted model system. Also, this is a result of the substituent size that provides a higher steric hindrance. In consequence the most stable conformation will need to distance more the cyano substituent respect to the other aromatic ring, increasing in this way the angle between the two aromatic rings and angle is shifting to  $45^\circ$  in the difluoro-substituted model system to  $50^\circ$  in the dinitrile-substituted model system. Another important aspect to comment is that there is an energy difference between the two minima of 2 kJ/mol, which is relatively high compared to the difference of almost 0 kJ/mol in the difluoro-substituted model system. This could be explained referring to the loss of planarity found in the aryl ring in the  $120^\circ$  conformation. Besides, this could be determinant for the Boltzmann populations, mismatching the population of the symmetrical angles.

Now, focusing to the energy curves related to the calculations with E-field applied, it's noticeable that the presence of the E-field is inducing more stable conformations by disfavoring

more the conformations that aren't minima than on the difluoro-substituted system, meaning that the effect of the E-field is more important. This behavior should be reflected into a higher selectivity on the most populated angle. This can be explained by the energy shift described on the first order approximation (see Equation 4). The shifting energy in this equation is provided by the  $-\vec{\mu} \cdot \vec{F}$  term, and as compared a situation with the same E-field, the only difference could be in the dipole moment. Before this comparison, it has to be known that the magnitude of the dipole moment of these molecules exhibit little variations in their different conformations, so it can be assumed that the magnitude of the dipole moment is always the same. The dipole moment of the difluoro-substituted system and dinitrile-substituted system is 1.06 a.u. (atomic units on dipole are equivalent to 0.39343 Debyes) and 2.82 a.u. respectively. This higher dipole moment makes the term  $-\vec{\mu} \cdot \vec{F}$  bigger and consequently the effect of the E-field is bigger to, shifting easier the more stable conformation at low E-fields by disfavoring more the angles near to the most stable angle.

Also, it has to be commented that the most stable conformations and the worst follow the same behavior as the model difluoro-substituted system. This is a result of the interplay between  $\pi$ -conjugation, steric hindrance and the E-field, showing a bigger trend to align the dipole moment with the E-field as stronger is the E-field. Even though, at the highest E-field calculated, the most stable angle in the dinitrile-substituted system isn't allowed to reach the  $10^\circ$  (is  $15^\circ$ ) due the higher steric hindrance of cyano respect to fluorine.

The symmetrical minimum it's also lost as on the difluoro-substituted because the breaking of the symmetry provided by the E-field, disappearing faster due to the higher dipole moment, consequence previously explained in this section. In conclusion, in this system there are significant shifts of the angle due to the E-field, which are similar to those in the difluoro-substituted system.

### 6.2.2. E-FIELD APPLIED CORRECTIONS ANALYSIS

Related to the energy corrections using the first order approximation (Equation 4) on the curves with E-field applied, can be observed in Figure 13 that follows the same trends as the difluoro-substituted system. A notable difference is that the correction doesn't exchange the relative stabilities between the two minima, so in consequence, the Boltzmann populations based on these corrections won't exchange the probabilities between the two minima as happens in the difluoro-substituted system providing an easier interpretation.

In order to analyze and compare better the magnitude order of the error committed by the first order approximation, it will be better to plot directly this error.

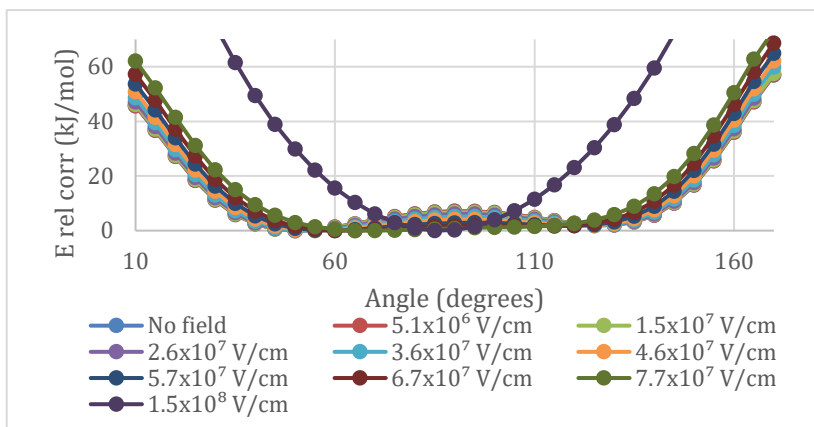


Figure 14. Zero-field and energy curves corrected by first order approximation.

As can be figured out in Figure 15, the trends that follows the error correction are exactly the same as in the difluoro-substituted system, but they are bigger at certain points.

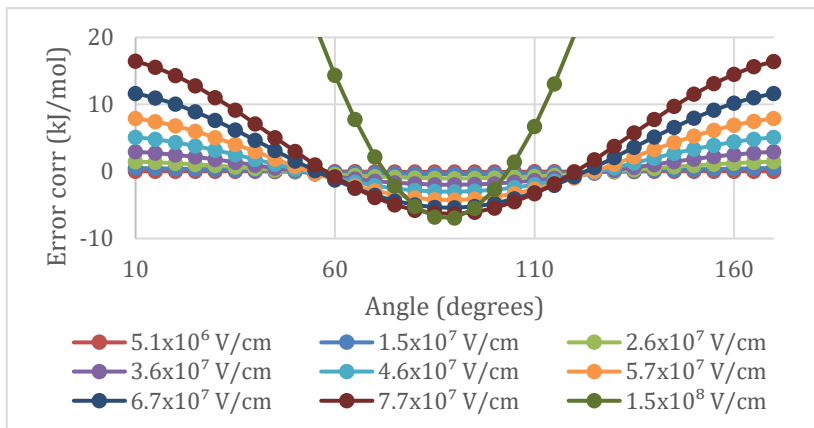


Figure 15. Error by using the first order approximation.

The maximums and minimums of the error takes higher values than in the difluoro-substituted case, providing a worst correction at those points. Because of this, the error at lower E-field is also higher compared to the difluoro-substituted system, concluding in general a worse validity of the first order approximation in this case. This worsening of the energy correction can be explained through the second term in Equation 3. Fluorine and cyano have the same amount

of negative charge, so the difference is their size. As cyano is bigger, this charge is distributed over more space than on fluorine, providing a higher polarizability and increases the second term of the energy, making it less negligible and producing a higher error by using the first order approximation. At this moment, it seems that fluorine is a better candidate to be used on the linker of the dimer of the 2D-CORF BB.

### 6.2.3. BOLTZMANN POPULATIONS ANALYSIS

Related to the Boltzmann populations at different temperatures, in the zero-field scenario (see Figure 16), the population of the stable conformation follows the same trend as on difluoro-substituted system while increasing the temperature. The main difference between the two model system variations is that on the dinitrile-substituted system, one of the symmetrical stable angles it's clearly more populated than the other. As it's mentioned on section 6.2.1, this is explained by the loss of symmetry of the aryl ring on the 120° conformation, increasing the gap energy between its symmetrical conformations. This extra stability of the conformation of 50° it's reflected in a higher angle population. Paying attention to the selectivity of the angle, if we figure out the addition of the populations of the two symmetrical angles, it can be concluded that there isn't a significant change.

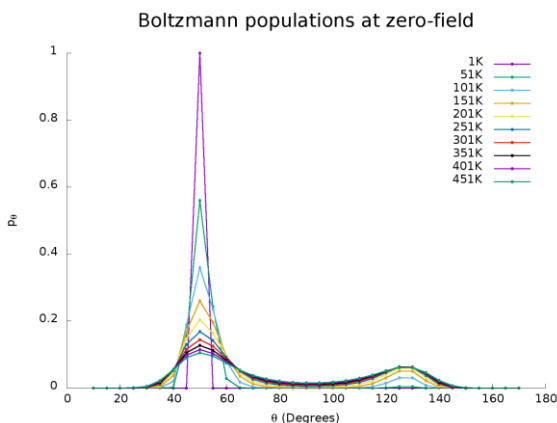


Figure 16. Probabilities to find a certain angle at a certain temperature at zero-field.

Related to the Boltzmann populations with the E-field applied (see Figure 17), we can observe that the behavior it's like the difluoro-substituted model system. As E-field is higher, the most populated angle is shifted to the most stable conformation at the corresponding E-field and increase the selectivity of the angle. In addition, at the higher temperature the selectivity is

worse because there is more thermal energy that helps to populate other conformations. Also, by comparing the two substitutions of the model system, the dinitrile-substituted system has a slightly higher selectivity at the same field, as was predicted in section 6.2.1. In conclusion, the effect of the E-field is more significant in the dinitrile-substituted model system than on the difluoro-substituted system because it can provide a better selectivity of the minimum angle.

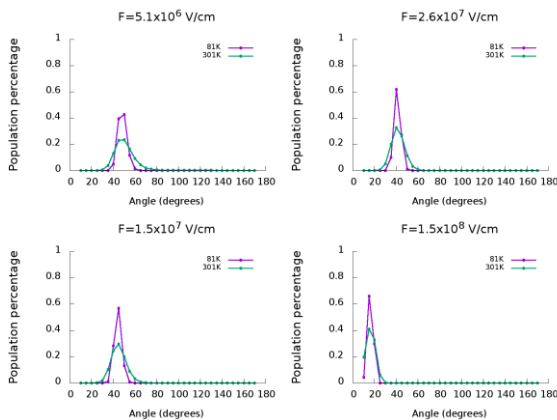


Figure 17. Probabilities to find a certain angle at a certain temperature with different E-fields.

#### 6.2.4. BOLTZMANN POPULATIONS CORRECTIONS ANALYSIS

Related to the Boltzmann populations corrections based on the E-field applied calculations on the dinitrile-substituted model system, we can expect that it will be less accurate than on the difluoro-substituted case because of the conclusion extracted on section 6.2.2. we know that the first order approximation is worst on the dinitrile-substitution.

As can be seen on Figure 17, these suspicions are confirmed. The amount population of the more stable angle compared with the zero-field populations at different temperatures is well represented by the first order approximation, but as happens on section 6.2.2. the most populated is shifted while E-field increases, shifting for example at  $6.7 \times 10^7$  V/cm from  $50^\circ$  to  $60^\circ$ , and increasing this shifting to almost perpendicularity at the highest extreme case of E-field.

In conclusion, the corrections of the Boltzmann populations are better on the difluoro-substituted system if the interpretation of the symmetrical angles are done: the corrections of the two systems represent well the amount of population, but on the dinitrile-substituted system,

the shifting of the most stable angle is higher at the same intensity of E-field. For now, fluorine it's a better candidate to be used in the calculation about the dimer of the 2D-CORF BB.

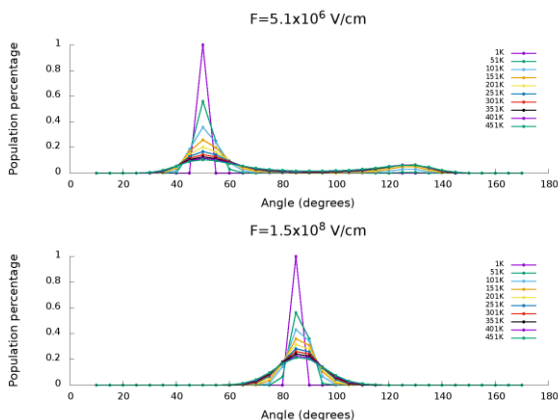


Figure 18. Probabilities to find a certain angle at a certain temperature based on the corrections of the first order dipolar contribution.

### 6.3. DIBROMO-SUBSTITUTED MODEL SYSTEM

In this section the calculation results of the dibromo-substituted model system will be comment and compared with those done on the difluoro-substituted and dinitrile-substituted systems. The main difference that bromine provides is a bigger size. As has been proved on dinitrile-substituted system, this will result into a higher steric hindrance and a higher polarizability, shifting the most stable angle and a getting worse the first order approximation respectively. Because of this, there is a high possibility that the dibromo-substitution will follow the same trends that the dinitrile-substitution respect to the difluoro-substitution, but higher because bromine is bigger than cyano.

#### 6.3.1. ZERO-FIELD AND E-FIELD APPLIED ANALYSIS

On the model system with two bromine substituents, 2,3-dibromobiphenyl at zero-field, has been found (see Figure 19) that the more stable angle of its conformation is  $90^\circ$ , without any symmetrical angle because it is just in the middle between  $10^\circ$  and  $170^\circ$ . This special angle is where steric hindrance is minimized, so it tells that the size of bromine plays a bigger role compared with the other substitutions studied and also it is coherent with the maxima localized at  $10^\circ$  and  $170^\circ$ . Furthermore, conformations near angles to  $90^\circ$  are relative stable too, showing

that, in this case, the  $\pi$ -conjugation is less important. Because of this increased range of stability, it is possible that the selectivity of the most population angle gets worse, distributing over the nearby angles.

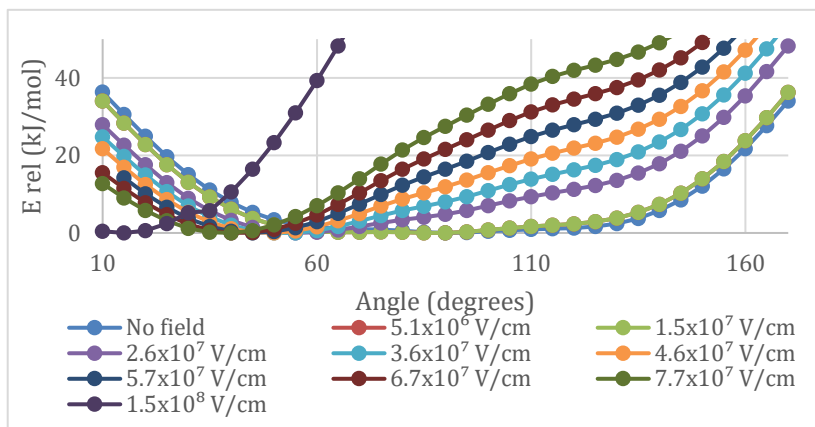


Figure 19. Zero-field and energy curves at different E-fields of dibromo-substituted model system.

When the E-field is applied (see Figure 19), indeed, as happens for the other substitutions, the most stable angle shifts in order to align the dipole moment of the system with the external E-field. In this case the shifting angle can be higher because the most stable conformation at zero-field is more distanced from the favorable alignment when the E-field is applied. As we can see, the depth of the minimum it's lower than the cyano-substituted system and similar to the difluoro-substituted system, which means the dipole moment is closer to the difluoro-substitution. Checking this value, the difluoro-substitution had a dipole moment of 1.06 a.u. while dibromo-substitution is 0.95 a.u., validating this prediction

### 6.3.2. E-FIELD APPLIED CORRECTIONS ANALYSIS

Related to the energy corrections on the curves with E-field applied, can be seen on Figure 20 that the shape of the corrections is pretty similar to the zero-field curve except the higher field curve.

Paying attention to the graph error in Figure 21, can be seen better the order of magnitude of the error committed by the first order correction of the dipole moment contribution. Compared to the systems previously commented in sections 6.1.2. and 6.2.2., the error of correction applied to the dibromo-substituted system is worse than on the difluoro-substituted system and



similar to the dinitrile-substituted system. As always, the correction works worse at higher E-fields.

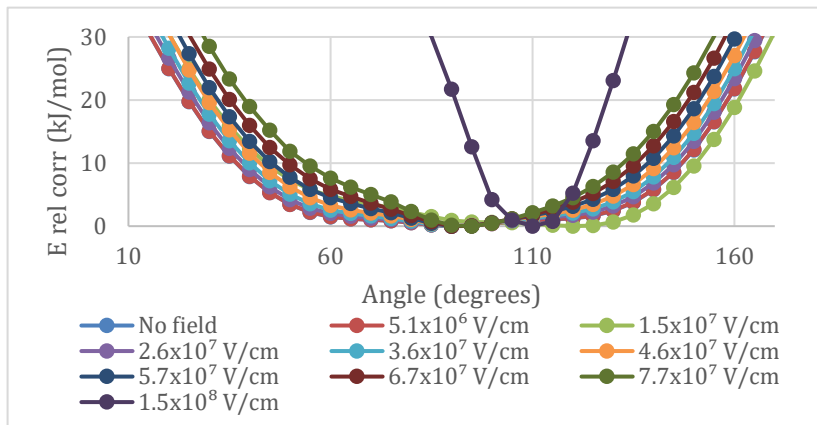


Figure 20. Zero-field and energy curves corrected by first order approximation.

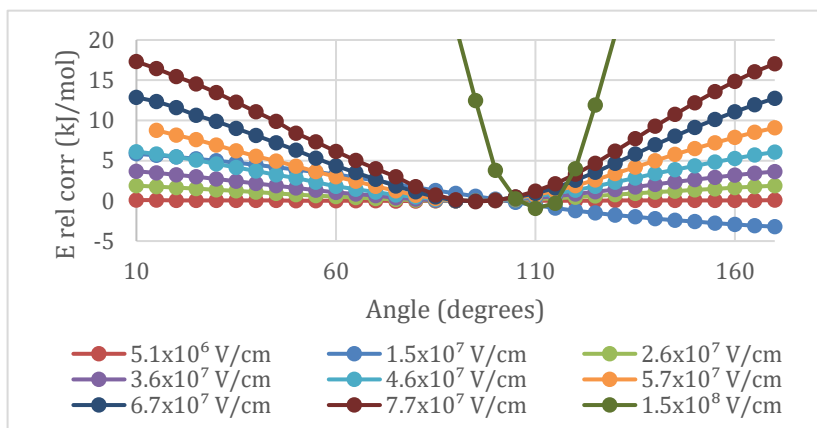


Figure 21. Error by using the first order approximation.

### 6.3.3. BOLTZMANN POPULATIONS ANALYSIS

Related to the Boltzmann populations at different temperatures at zero-field, what was expected on section 6.3.1. is what is seen on the Figure 22.

The most populated angle is the most stable, but due to the proximity in energy with the nearby angles, these can be populated, giving rise to a poor selectivity for the 90° conformation for even relatively low temperatures.

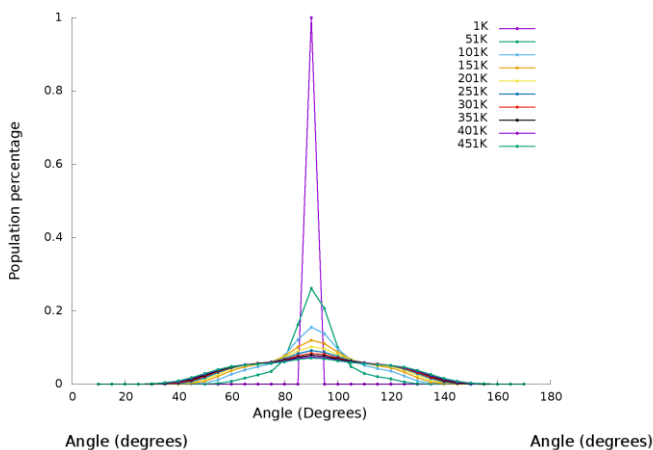


Figure 22. Probabilities to find a certain angle at a certain temperature at zero-field.

When an E-field is applied, the consequences of the energy curves of this are manifested into a poor selectivity. The low dipole moment of the molecule (compared with the other disubstitutions) doesn't stabilize enough the minimum and the same happens as at zero-field which gives rise to a worse selectivity on the most populated angle, especially at low E-fields. Compared with the other considered di-substitutions this one is the worst, because the E-field needed to reach a certain selectivity is higher, providing a worse sensitivity.

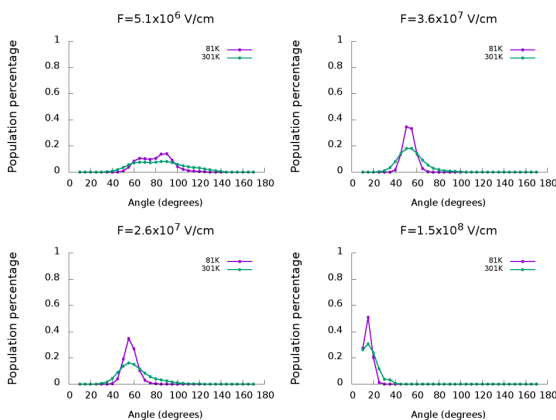


Figure 23. Probabilities to find a certain angle at a certain temperature with different E-fields.

### 6.3.4. BOLTZMANN POPULATIONS CORRECTIONS ANALYSIS

Now, the corrections of the Boltzmann populations based on the calculations with the E-field applied are shown. At some E-fields, the most populated angle is shifted, reaching 30° of shift. Also, at higher E-fields the sharp distribution of the population is lost. It can be seen quickly that this correction based on the first order approximation doesn't work well while bromine is the substituent on the model system. We thus discard this atom choice to be used on the linker of the dimer of the 2D-CORF BB. Following the conclusion on section 6.2.2. that fluorine was a better candidate than cyano for the study, it is concluded that the chosen atom for the final study of the 2D-CORF BB dimer will be fluorine.

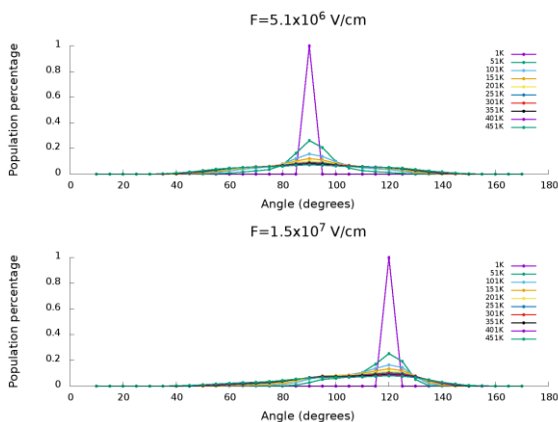


Figure 24. Probabilities to find a certain angle at a certain temperature based on the corrections of the first order dipolar contribution.

## 6.4. DIMER OF THE 2D-CORF BB

### 6.4.1. ZERO-FIELD SINGLET AND TRIPLET STATES ANALYSIS

In this section starts the study of the dimer of the 2D-CORF BB, whose linker will be substituted by two fluorine atoms, chosen through the previous studies using the model system. Because of the two unpaired electrons in the radical BBs, there are two possible states of the dimer: one with the two spins pointing in the same direction (triplet) and the other pointing into opposite directions (singlet). The energy curves at zero-field of the two states have been calculated (see Figure 25), defining the 0° when the aromatic ring of the linker is coplanar to the aC planes.

As can be seen, all conformations are near in energy. This is because of two factors. The first one is that there isn't any steric hindrance that affects the rotation of the linker. This absence of steric hindrance is provided by the triple bonds, who add a high distance between the linker and the TAMs. The other factor also is provided by the triple bonds: these have two orthogonal  $\pi$ -systems and then, the conformation of the linker could be stabilized by  $\pi$ -conjugation at  $0^\circ$  and at  $90^\circ$  (symmetrical too), angles where are localized the energy minima of the molecule. In all the intermediate situations, the  $\pi$ -conjugation of the dimer is still notable, because always will be a certain percentage of  $\pi$ -systems overlapping. In consequence, all the possible angles are more or less stabilized by  $\pi$ -conjugation and then the energy curve is very flat. Due to difficulties in obtain a perfectly symmetric molecular conformation of the BBs, appears a maximum at  $180^\circ$  where a minimum is expected.

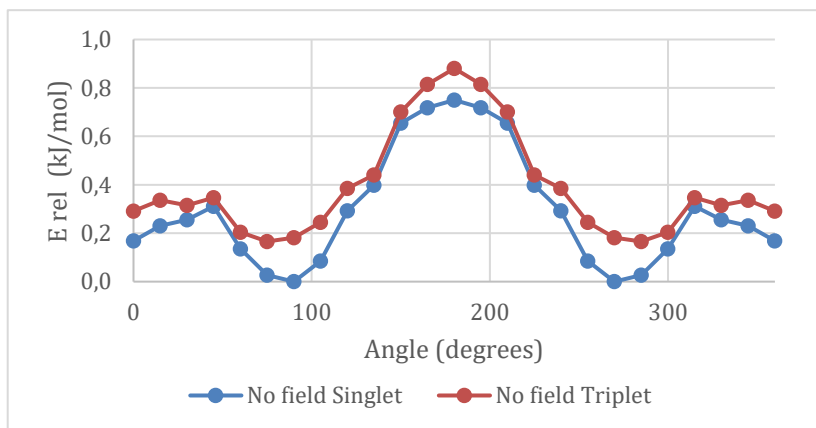


Figure 25. Zero-field singlet and triplet states energy curve of the dimer of the BB 2D-CORF.

Comparing the relative stability between singlet and triplet states, can be seen that the singlet state is always the ground state at any conformation. The lower energy of the singlet state is because of the high  $\pi$ -conjugation of the dimer: the two unpaired electrons could be in the same  $\pi$ -orbital that involves all the molecule, reducing in this way the electrical repulsion between them. Because of this higher stability of the singlet state, it's reasonable that the predictions using the first order approximation (previously validated) of the behavior of the 2D-CORF dimer in an E-field will be done in this multiplicity state (section 6.4.3.).

#### 6.4.2. MAGNETIC INTERACTIONS ANALYSIS

In this section it will be checked the dependence on the conformation of the linker with respect to the magnetic interactions, whose strength is proportional to the energy gap between triplet and singlet state. This energy gap will be calculated by subtracting the triplet state energy curve to the singlet state one.

As can be seen on Figure 26, the energy gap is different by changing the conformation of the molecule, meaning that the strength of the magnetic interactions is change through the rotation of the linker that has been used in this study.

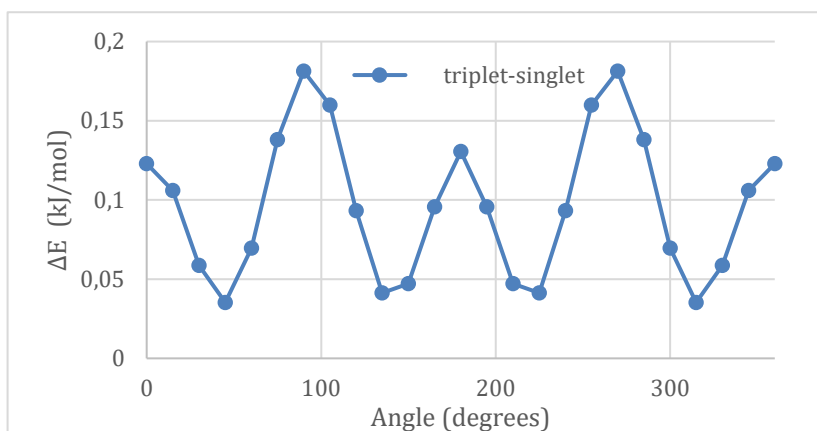


Figure 26. Energy gap between triplet and singlet state of the dimer of the BB 2D-CORF.

In order to analyze the strength of the magnetic interactions, the value of the biggest energy gap of all the rotation of the linker, at  $90^\circ$  (the same that the symmetrical angle), are compared with other values. Definitely, changes in magnetic properties will be small but measurable. This is a proof of principle that magnetic interactions can be tuned by controlling the conformation of the system.

### 6.4.3. PREDICTIONS OF THE EFFECT OF AN E-FIELD THROUGH THE FIRST ORDER APPROXIMATION

In this section, the first order approximation will be used to predict the conformation stability of the linker while an E-field is applied on the dimer of the 2D-CORF BB on the singlet state. In this case, using the knowledge acquired by studying the model system will be used to choose an E-field direction that targets the linker conformation related to the strongest magnetic interactions,  $90^\circ$ . As has been seen through the analysis of the model system, when an E-field is applied the trend is to align the dipole moment with this E-field. In order to reach the

alignment at  $90^\circ$ , figuring out that the direction of the dipole moment is pointing to the intermediate space between the two fluorine atoms and parallel to the aromatic ring of the linker, the E-field must be applied orthogonal to the  $\alpha\text{C}$  planes of the dimer. The calculations by using the first order approximation will be done in a similar way to those that have been done using the corrections calculations done in the analysis of the model systems. The scalar product between the dipole moment and the E-field will be calculated, and this will be subtracted from the energy at zero-field.

The predictions will be done in a range that has been proved that works well: between  $5.1 \times 10^6$  V/cm and  $3.6 \times 10^7$  V/cm. On this range, the maximum error found on the calculations of the difluoro-substituted model system is less than 1 kJ/mol and the Boltzmann populations are well represented (could be an exchange of the symmetric conformations, but this does not affect the interpretation).

As can be seen in Figure 27, that the  $90^\circ$  conformation is stabilized by the effect of the external E-field as, achieving the target conformation of the study and consequently inducing a specific strength of magnetic interactions. One the other hand, the energy difference of the minimum with respect conformations at nearby angles isn't very high, and this could be a problem, providing a poor selectivity of the population of the angle at different temperatures. Indeed, the angle conformation with the highest dipole moment of the molecule is  $0.84$  a.u. ( $75^\circ$ ), which is a low value, related to poor angle population selectivities.

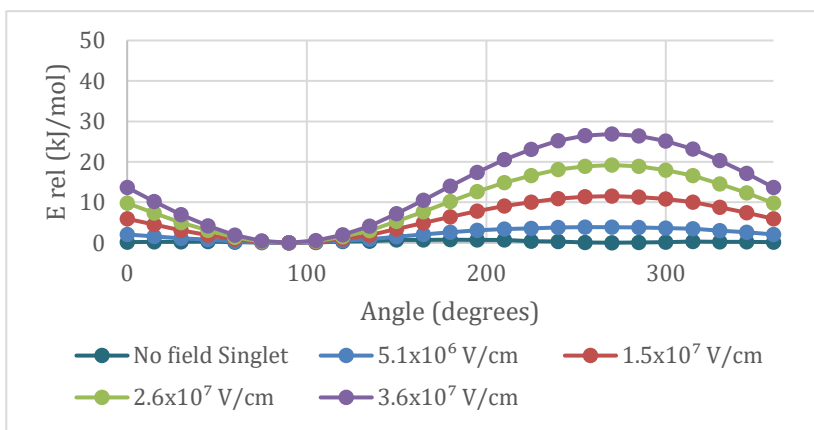


Figure 27. Energy curves at different E-fields predicted by using the first order on the dimer of the BB 2D-CORF.

#### 6.4.4. PREDICTIONS OF BOLTZMANN POPULATIONS WITH AN E-FIELD THROUGH THE FIRST ORDER APPROXIMATION

In this section, the Boltzmann populations will be calculated based on the prediction of the energy curve of the rotation of the linker with an E-field applied. The calculations of the Boltzmann populations will be done using the same program that has been used for the model system calculations.

The populations of the conformations at the different intensities of E-field are plotted on Figure 28. Can be seen, the selectivity at  $90^\circ$  is reduced the population of the nearby conformations, as was expected on section 6.4.2., but despite this good selectivities are achieved, being 50% the best, at the  $90^\circ$  conformation on nitrogen liquid temperature an applying a field of  $3.6 \times 10^7$  V/cm.

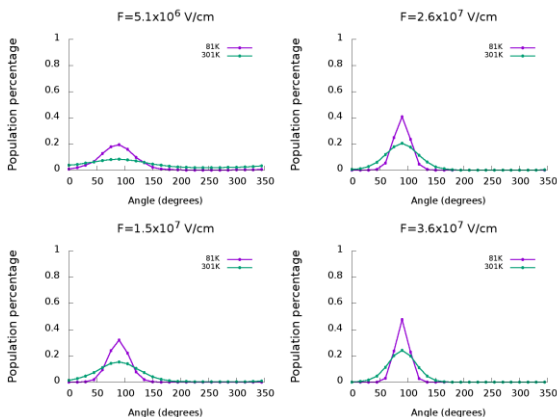


Figure 28. Boltzmann populations at different field predicted by using the first order approximation of the dimer of the BB 2D-CORF.





## 7. CONCLUSIONS

The most stable conformation of the model system depends on their substitution: 45° for difluoro-substitution, 50° for dinitrile-substitution and 90° for dibromo-substitution.

The most stable conformation of the model system is a result of an interplay between steric hindrance and  $\pi$ -conjugation.

An E-field applied in the correct direction can shift the angle of the most stable conformation of any variation studied of the model system: the needed intensity of E-field to induce a shift on the conformation depends mainly of the dipole moment.

In the model system, the first order approximation works better when the polarizability of the substituents is smaller. Also, the validity of the first order approximation works better at lower E-fields.

Fluorine is the best option among the studied options for substitution on the linker of the dimer of the BB 2D-CORF: the first approximation can be used with at  $3.6 \times 10^7$  V/cm with a precision of 1kJ/mol.

The dimer of the BB 2D-CORF is more stable when the linker is coplanar to the extended network and when is perpendicular to the network.

Different conformations of the linker of the dimer are related to different magnetic interactions strengths, which are low but measurable in this study.

An E-field applied in the right direction can shift the linker conformation of the dimer into a target conformation.

A 50% of linker conformation selectivity can be achieved at liquid nitrogen temperature by applying an  $3.6 \times 10^7$  V/cm E-field.



## 8. REFERENCES AND NOTES

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## 9. ACRONYMS

2D: Two dimensional.

COF: Covalent Organic Framework.

CORF: Covalent Organic Radical Framework.

BB: Building Block

TAM: Triarylmethyl.

E-field: Electric Field.

DFT: Density Functional Theory.

V: Volt.

cm: Centimetre.

K: Kelvin.

a.u.: Atomic Units.



# APPENDICES





## APPENDIX 1: DIFLUORO-SUBSTITUTED MODEL SYSTEM Z-MATRIX OF THE STANDARD SCANNING.

0 1

C

C 1 Da01

C 1 Da02 2 Aa01

C 1 Da03 2 Aa02 3 Ha01

C 2 Da04 1 Aa03 3 Hscan

C 2 Da05 1 Aa04 5 Ha02

C 3 Da06 1 Aa05 2 Ha03

C 4 Da07 1 Aa06 2 Ha04

C 5 Da08 2 Aa07 1 Ha05

C 6 Da09 2 Aa08 1 Ha06

C 7 Da10 3 Aa09 1 Hb01

C 9 Da11 5 Aa10 2 Hb02

H 3 Db01 1 Aa11 2 Hb03

H 4 Db02 1 Aa12 2 Hb04

F 5 Dc01 2 Aa13 1 Hb05

H 6 Db03 2 Aa14 1 Hb06

H 7 Db04 3 Aa15 1 Ha07

H 8 Db05 4 Aa16 1 Ha08

F 9 Dc02 5 Aa17 2 Ha09

H 10 Db06 6 Aa18 2 Ha10

---

H	11	Db07	7	Aa19	3	Ha11
H	12	Db08	9	Aa20	5	Ha12

Da01=1.484492

Da02=1.399352

Da03=1.398276

Da04=1.404950

Da05=1.398550

Da06=1.391444

Da07=1.393153

Da08=1.397040

Da09=1.389980

Da10=1.394615

Da11=1.392632

Db01=1.087152

Db02=1.087383

Db03=1.086664

Db04=1.087521

Db05=1.086793

Db06=1.086287

Db07=1.087008

Db08=1.085295

Dc01=1.363

Dc02=1.363

Aa01=120.0

Aa02=120.0

Aa03=120.0

Aa04=120.0

Aa05=120.0

Aa06=120.0

Aa07=120.0

Aa08=120.0

Aa09=120.0

Aa10=120.0

Aa11=120.0

Aa12=120.0

Aa13=120.0

Aa14=120.0

Aa15=120.0

Aa16=120.0

Aa17=120.0

Aa18=120.0

Aa19=120.0

Aa20=120.0

Ha01=180.0

Ha02=180.0

Ha03=180.0

Ha04=180.0

Ha05=180.0

Ha06=180.0

Ha07=180.0

Ha08=180.0

Ha09=180.0

Ha10=180.0

Ha11=180.0

Ha12=180.0

Hb01=0.0

Hb02=0.0

Hb03=0.0

Hb04=0.0

Hb05=0.0

Hb06=0.0

Hscan=10.0 S 32 5.0

## **APPENDIX 2: STANDARD SCANNING OF THE DIFLUORO-SUBSTITUTED MODEL SYSTEM INPUT APPLYING AND E-FIELD**

```
%chk=/home/g2invitado2/kilian/bifenil/F/fields/x/x130.chk
```

```
#p opt=(Z-matrix,MaxStep=8,MaxCycles=200) UPBE1PBE/6-31+g(d) Field=x+130 NoSymm  
scf=Tight
```

Scanx130

z-matrix (see Appendix 1)



## APPENDIX 3: PROGRAM USED TO CALCULATE THE BOLTZMANN POPULATIONS

PROGRAM analisi\_poblacional

!Aquest programa calcula la distribució del boltzmann d'una poblacio puntual

IMPLICIT NONE

INTEGER :: fStat, nPoints

integer :: i

REAL :: t !temperatura d'anàlisi

REAL, ALLOCATABLE, DIMENSION(:) :: factor, p, E !factor de boltzman= $\exp(-E_i/(k_B*t))$ ,  
probabilitat i energies.

REAL(8) :: z ! funció de partició.

REAL,PARAMETER :: R = 8.3144621E-3 ! Buscar la constant de boltzman en  
kJ mol

CHARACTER(3), ALLOCATABLE, DIMENSION(:) :: angle

CHARACTER (24) :: fName

CALL get\_command\_argument(1, fName, status=fStat)

if (fStat == 0) then

print\*, '1'

```
        OPEN(unit=1, file=trim(fName), status='old')
ELSE
    print*, '2'
    CALL exit()
END IF

READ(1,*) nPoints, t

ALLOCATE(factor(nPoints), p(nPoints), E(nPoints), angle(nPoints))

DO i = 1, nPoints, 1
    READ(1,*) angle(i), E(i)
    factor(i)= exp(-E(i)/(R*t))
END DO

z=sum(factor)

OPEN(2,file='out.out')!, status='new')

DO i =1, nPoints, 1
    p(i)=factor(i)/z
    write(2,*) angle(i), p(i)
END DO

END PROGRAM analisis_poblacional
```



