

**Ministry of Higher Education and Scientific Research**



**University Abbés Laghrour Khenchela**  
**Faculty of Science and Technology**  
**Department of Matter Sciences**



N°: .....

## **Thesis**

Presented to obtain the master's degree

**In Chemistry**

**Speciality: Analytical Chemistry**

Thesis entitled :

**Substitution effect on electronic and  
spectroscopic properties of benzofuran-2-  
carboxylic acid**

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"قال تعالى: "وَلَقَدْ آتَيْنَا لُقْمَانَ الْحِكْمَةَ أَنِ اشْكُرْ لِلَّهِ ۚ وَمَن يَشْكُرْ فَإِنَّمَا يَشْكُرُ لِنَفْسِهِ ۖ وَمَن كَفَرَ فَإِنَّ اللَّهَ غَنِيٌّ حَمِيدٌ (١٢)"  
قال رسول الله صل الله عليه وسلم: " من لم يشكر الناس، لم يشكر الله عز وجل" رواه أحمد وأبو داود والبخاري

أولا وقبل كل شيء، الحمد لله الذي بنعمته تتم الصالحات، الحمد لله الذي وفقنا وأعاننا على إتمام هذا العمل المتواضع.  
راجين من الله عز وجل أن يكون هذا البحث العلمي ارثا يستفاد منه في المشوار العلمي

We would like to express our sincere gratitude to our supervisor Mrs. Hakkar Farida. Throughout this research work, she has provided us with a deeper understanding of the various aspects of the subject.

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I also do not forget those who taught me in all phases.  
Especially Mr. Kertiou Noureddine.



# *Dedication*

*\* To my father Bachir*

*\* To my mother Albaidha,*

*\* To my brother Abd arrazak,*

*\* To my brother Mohamed alamin,*

*\* To my only sister Sara,*

*\* To all who supported me,*

*\* To all my friends and colleagues,*

*\* To ROMAÏSSA.B AND ROFAIDA.F,*

*\* To my family.*

*Hadidi Rogiya*

اهدي تخس جي هذنا:

الى من ريدياني وكبراني وعلما ني اولى الخطوات للمضي قلما:

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الى من كانت بمثابة الأمر الثانية، أختي الغالية أدامك الله لها

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الى من كن لي أخوات قبل أن يكن صديقات: بن دبكة، غفران، حليدي

مرقيته، طراذي نجاة، مومن وفاء... أحبكن في الله

الى من ساندوني وأيدوني ومنحوني من عطائهم وكن همي

*Faghi Rofaida*

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## List of acronyms

Abbreviation	Description
ADF	Amsterdam Density Functional
AO	Atomic Orbital
DFT	Density Functional Theory
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
MO	Molecular Orbital
FMO	Frontier Molecular orbitals
BP86	Becke Perdew 86
UV -Vis	Ultraviolet Visible
TDDFT	Time-Dependent Density Functional Theory

# **GENERAL INTRODUCTION**

## General Introduction

Benzofurans have attracted a great deal of interest because of their presence in a large number of natural products, their biological activities, and their potential applications as pharmacological agents. There are an amazing number of approved benzofuran-containing drugs in the market as well as compounds currently going through different clinical phases or registration statuses. Due to the wide range of biological activities of benzofurans, their structure activity relationships have generated interest among medicinal chemists [1].

Particularly, Benzofuran-2-carboxylic acid and its derivatives are very important and are widely used as starting compounds in the synthesis of pharmaceuticals. It was used to synthesize cathepsin K inhibitors (azepinone and methyladenine), dopamine (endogenous ligand for dopamine receptors), and chromans [2].

The objective of this work is to show the substituent effects on geometrical parameters and electronic properties of benzofuran-2 carboxylic acid molecule substituted by OH, NH<sub>2</sub>, Cl, CH<sub>3</sub> at different position of the phenyl or furan rings.

This manuscript is divided into three chapters:

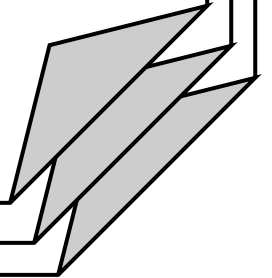
As the results described in this manuscript are based on Benzo[b]furan carboxylic acids derivatives and its electronic spectra, we will be devoted the first chapter to general information on Benzo[b]furan carboxylic acids and its derivatives and to Theoretical Foundations of UV-Visible Spectroscopy

Chapter two is devoted to calculate the geometrical parameters as well as the electronic properties (HOMO-LUMO, dipole moment and hirshfeld charge analysis) of Benzofuran-2-carboxylic acid and its substitutes

In chapter three, the optimized geometries of Benzofuran-2-carboxylic acid and its derivatives allowed to predict the UV-Vis spectra and to identify the spectral position and the nature of the different electronic transitions according to their molecular orbital localization

# **CHAPTER I**

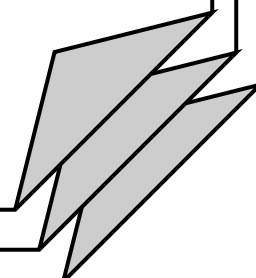
## **Bibliographic reminder**



# **CHAPTER I**

## **Part A**

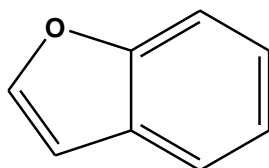
### **General information on Benzo [b]furan carboxylic Acids**



**I-Introduction**

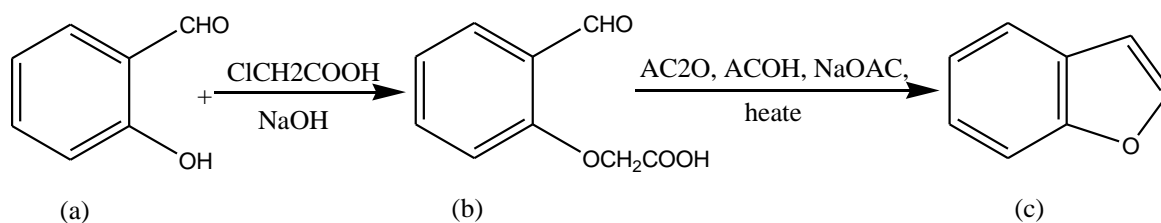
Benzofuran skeleton holds an important position in organic chemistry and it is considered one of the most important heterocyclic systems because of its diverse profile of biological activity. This structural unit is among feasible potent active inhibitors against many diseases, viruses, microbes, fungus and enzymes [3].

Benzofuran is a linear two ring heterocyclic compound. As the name implies, consisting of a benzene ring fused to a furan ring (see scheme 01).



**Scheme 01:** Chemical Structure of Benzo[b]furan

As shown in Scheme 02, reaction of salicylaldehyde (a) with chloroacetic acid [4] gives o-formyl phenoxy acetic acid (b). When refluxed with acetic anhydride in glacial acetic acid, it affords Benzo[b]furan (c)



**Scheme 02.** Synthesis of Benzo[b]furan [5]

Over the time, benzofuran derivatives have attracted many researchers due to the broad scope of their biological activity, which include anticancer, antimicrobial, antioxidant and anti-inflammatory [6]. Among these derivatives, Benzofuran carboxylic acids which is the subject of our study.

## II- Benzo [b]furan carboxylic Acids

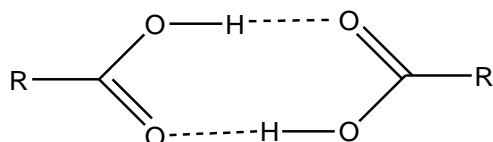
### II.1-Carboxylic acids

Carboxylic acids are organic acids characterized by the presence of at least one carboxyl group. The general formula of a carboxylic acid is R-COOH [7]. Acids with two or more carboxyl groups are called dicarboxylic, tricarboxylic, etc.

Because they are both hydrogen-bond acceptors (the carbonyl) and hydrogen-bond donors (the hydroxyl), they also participate in hydrogen bonding. Together the hydroxyl and carbonyl group form the functional group carboxyl

Carboxylic acids are typically weak acids, meaning that they only partially dissociate into  $H^+$  cations and  $RCOO^-$  anions in neutral aqueous solution. Deprotonation of a carboxylic acid gives a carboxylate anion, which is resonance stabilized because the negative charge is shared (delocalized) between the two oxygen atoms increasing its stability. Each of the carbon-oxygen bonds in a carboxylate anion has partial double-bond character [8].

Carboxylic acids usually exist as dimeric pairs in nonpolar media due to their tendency to “self-associate.”

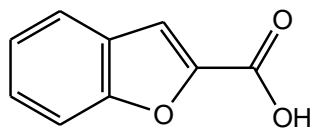


**Scheme 03.** Carboxylic acids dimers

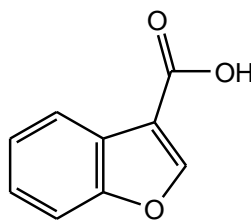
### II.2- isomers of Benzo [b]furan monocarboxylic acid

The Benzofuran carboxylic acids, having the carboxy substituent in different position of the Benzofuran skeleton as shown in scheme 5, obtained either by:

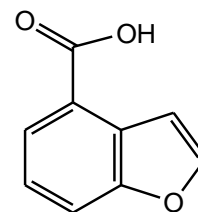
- Haloform reaction;
- Dehydrocyclization of butanone;
- Hydrolysis of the appropriate esters.



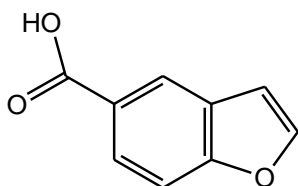
Benzo[2,3-b]furan-2-carboxylic acid



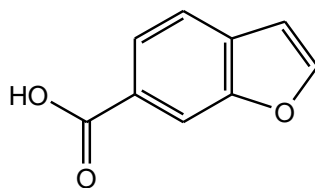
Benzo[2,3-b]furan-3-carboxylic acid



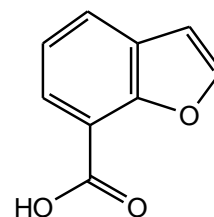
Benzo[2,3-b]furan-4-carboxylic acid



Benzo[2,3-b]furan-5-carboxylic acid



Benzo[2,3-b]furan-6-carboxylic acid

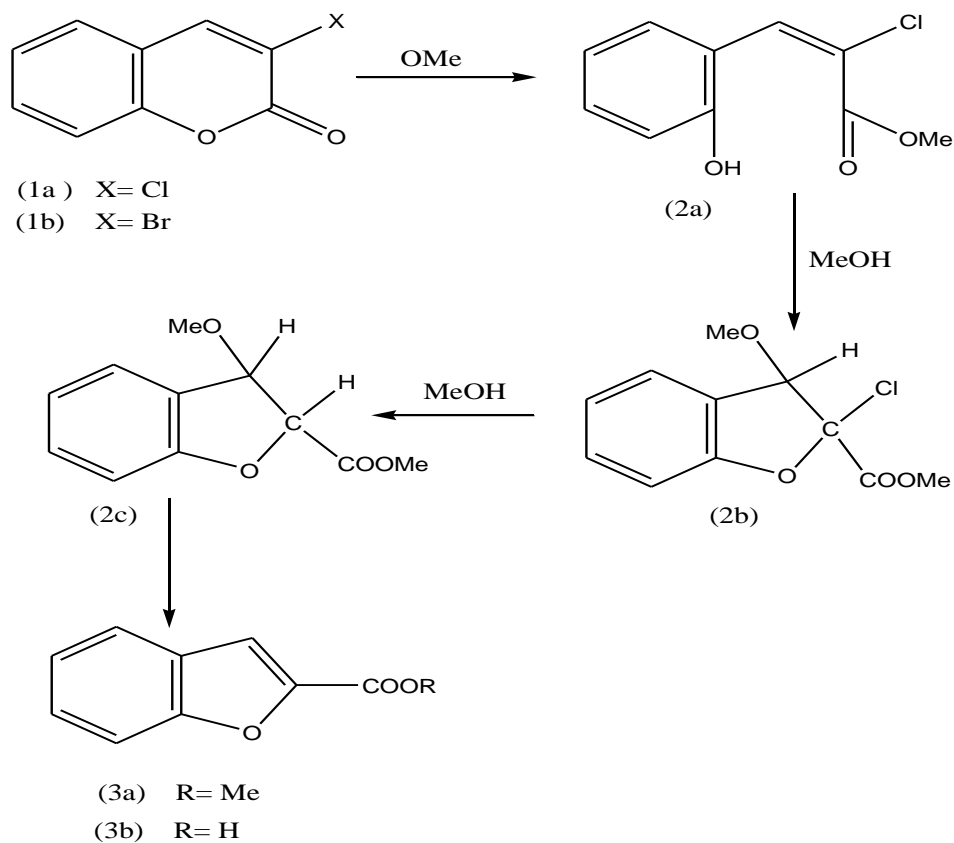


Benzo[2,3-b]furan-7-carboxylic acid

**Scheme 04:** Different isomers of Benzo[2,3-b]furan monocarboxylic acid

### II.3-Preparation of 2-benzofurancarboxylic acid

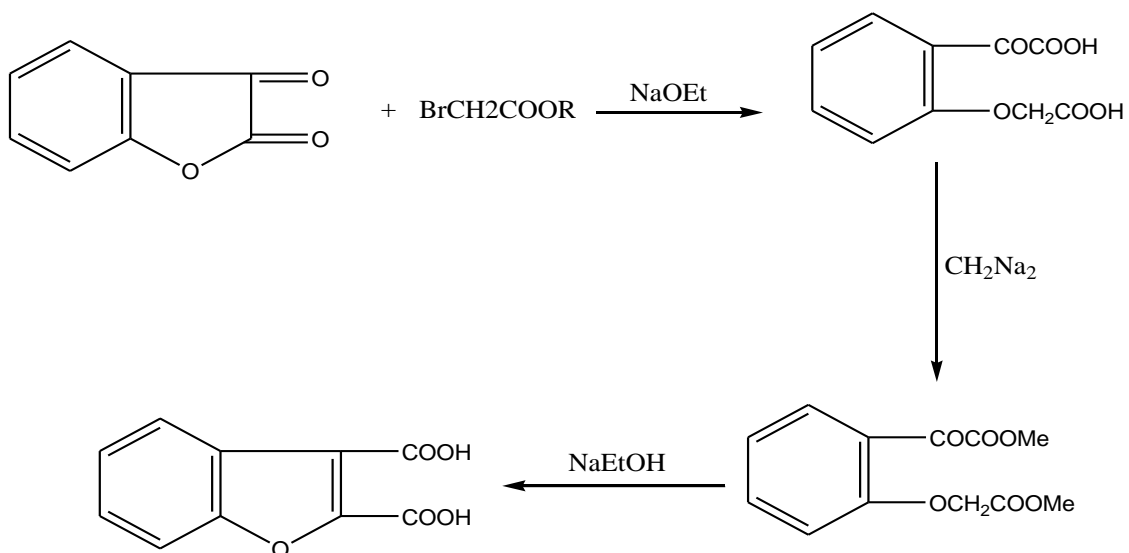
The preparation of 2-benzofurancarboxylic acid from coumarin was made by Perkin's discovery, when the 3-halocoumarin (1b) heated with Alkali gave (3b). The reaction of 3-chlorocoumarin with sodium methoxide produces methyl 2-benzofurancarboxylate only if methanol is present. It is postulated that the methoxide ion attacks the carbonyl group of 1a to yield a phenoxide ion (2a). A Michael addition of methanol to the double bond of 2a (or its conjugated acid) gives an intermediate 2b, which has a sp<sup>3</sup> carbon-bearing chlorine which could then undergo an intermolecular displacement easily to yield 2c. This would be followed by loss of methanol to afford 3a. [9]



**Scheme 05.** Synthesis of 2-benzofurancarboxylic acid [10]

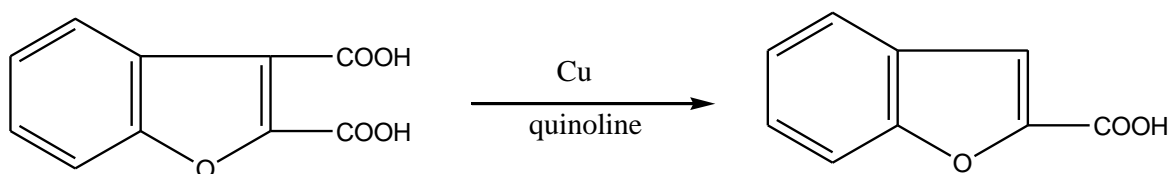
#### II.4-Benzo[b]furan dicarboxylic acid

The Benzo furan dicarboxylic acid was obtained from benzofuran-2,3-dione by the sequence of reactions illustrated in the equations below



**Scheme 06.** Synthesis of benzofuran-2,3-dicarboxylic acid [11]

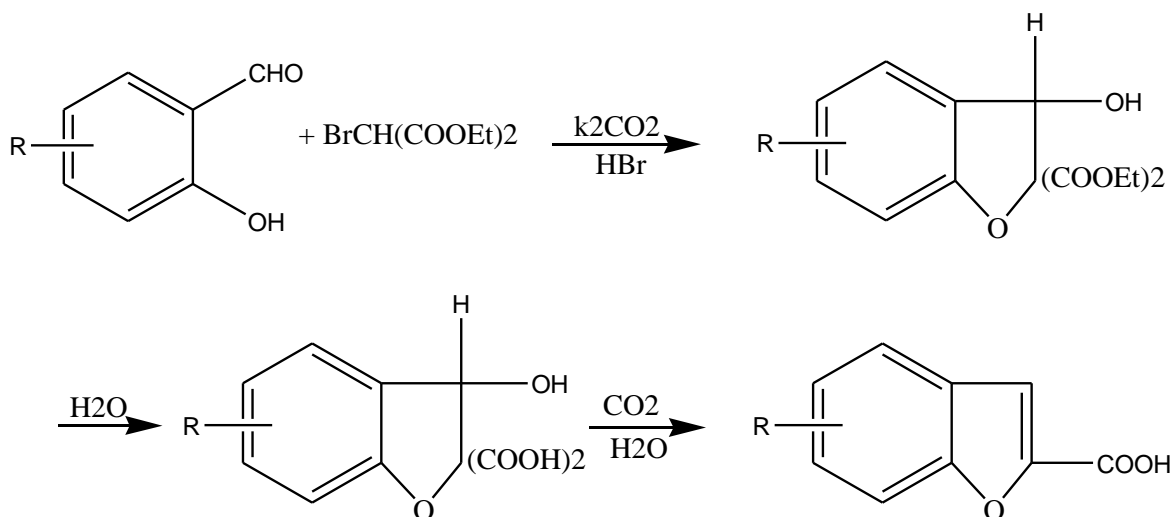
In the presence of copper and quinoline, we can obtain the Benzofuran-2-carboxylic acid as shown in scheme 07.



**Scheme 07.** Preparation of benzofuran-2- carboxylic acid from benzofuran-2,3-dicarboxylic acid [11]

### III-Substituted derivatives of 2-benzofurancarboxylic acid

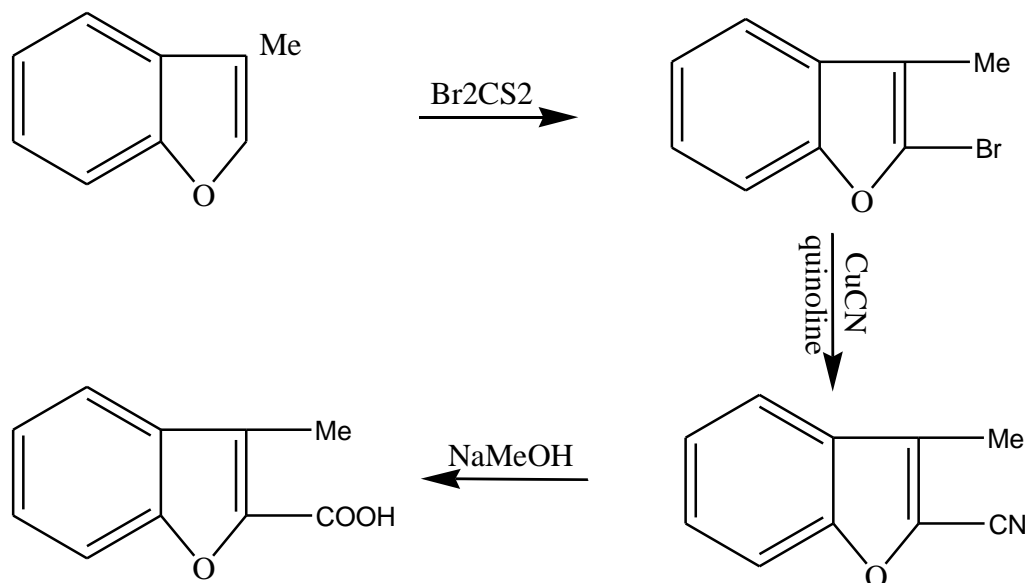
An appropriate method for the preparation of substituted derivatives of 2-benzofurancarboxylic acid is the condensation of o-hydroxy benzaldehydes with ethyl bromo malonate in the presence of potassium carbonate as show in scheme 8



**Scheme 08.** Preparation of different substituted derivatives of 2-benzofurancarboxylic acid [12]

#### III.1- 3-Methylbenzofuran-2-carboxylic acid

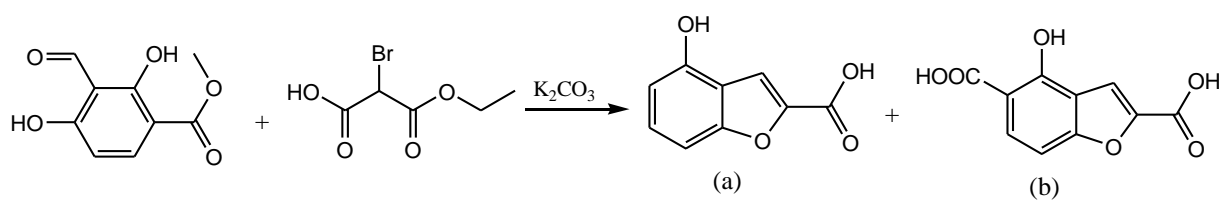
3-Methylbenzofuran-2-carboxylic acid was obtained by the sequence of reactions as shown in Scheme 9.



**Scheme 09.** Synthesis of 3-Methylbenzofuran-2-carboxylic [12]

### III.2- 4-hydroxybenzofuran-2-carboxylic acid

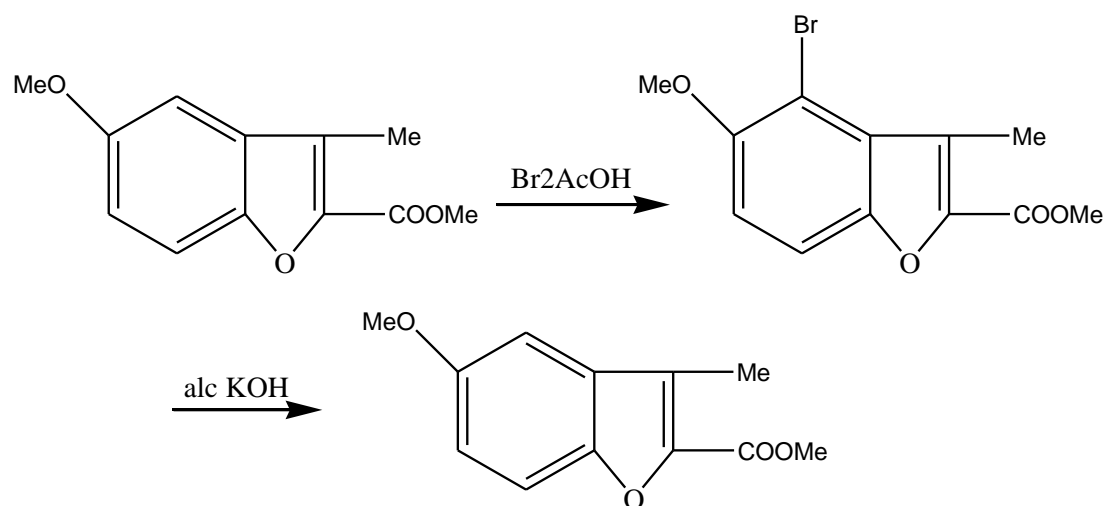
Condensation of 2,6-dihydroxy-3-methoxybenzaldehyde with ethyl bromo malonate in presence of potassium carbonate yields a mixture of 4-hydroxybenzofuran-2-carboxylic acid (a) and 4-hydroxybenzofuran-2,5-dicarboxylic acid (b)



**Scheme 10.** Synthesis of 4-hydroxybenzofuran-2-carboxylic acid [13]

### III.3- 5-methoxy-3-methylbenzofuran-2-carboxylic acid

The equation below (Scheme 11) shows the preparation of one of the substituted derivatives of 2-benzofurancarboxylic acid

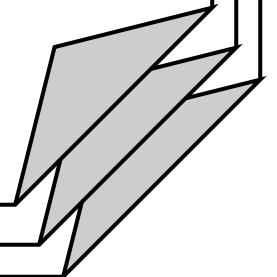


**Scheme 11.** Synthesis of 5-methoxy-3-methylbenzofuran-2-carboxylic acid [14]

# **CHAPTER I**

## **Part B**

### **Theoretical Foundations of UV-Visible Spectroscopy**



## I-Introduction

Molecular absorption spectroscopy UV-Visible is a technique for the qualitative and especially quantitative analysis of inorganic and organic species. It is a fast-analytical technique that measures the absorbance or transmittance of light [15]. Although the UV wavelength ranges from 100 nm to 380 nm and the visible component goes up to 800 nm [16], most of the spectrophotometers have a working wavelength range between 200 nm and 1100 nm. The spectral range corresponding to the UV-Vis light from 100 nm to 200 nm does not have much practical usefulness because it is vacuum UV light and above 800 nm, it is considered infrared light. The ability of matter to absorb and to emit light is what defines its color and the human eye is capable of differentiating up to 10 million unique colors

UV-Visible spectroscopy is based on the Bohr-Einstein frequency relationship given by the following equation:  $\Delta E = E_2 - E_1 = h\nu$  (I)

The equation I links the molecular energy states  $E_i$  with the frequency  $\nu$  of the electromagnetic radiation.

$h$  is Planck's constant of  $6.626 \times 10^{-34}$  Js.

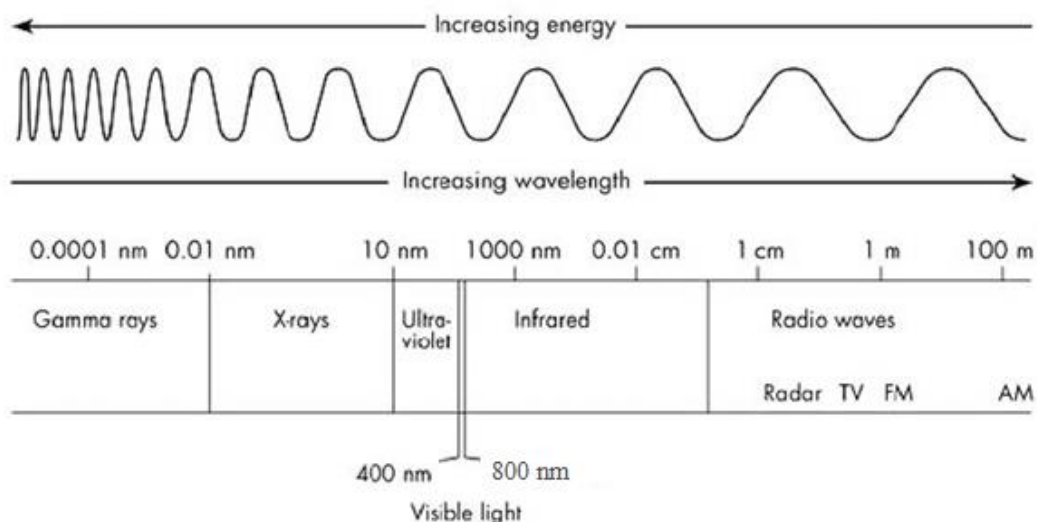


Figure 1: The electromagnetic spectrum diagram with wavelengths

The absorption of radiation by the molecule occurs when the frequency of the incoming light is equal to the energy difference between a molecule's ground and excited states. The excitation of an electron from the ground state to the excited state is an electronic transition (Figure 2).

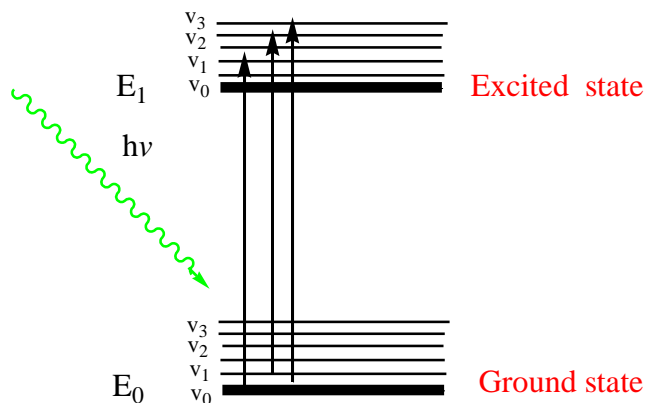


Figure 2: Absorption excitation of an electron

## II-Lambert-Beer law

The Lambert Beer law forms the mathematical-physical basis of light absorption measurements (figure 2) on gases and solutions in the UV-Vis and IR regions [17].

When passing through a transparent cuvette filled with sample solution, the light intensity is attenuated proportionally to the sample concentration. In other words, a higher concentrated sample solution will absorb more light. In addition, the attenuation is also proportional to the length of the cuvette; a longer cuvette will lead to a higher absorption of light.

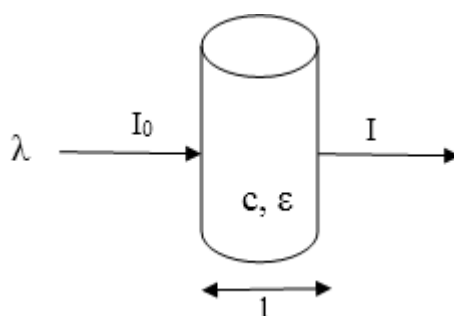


Figure 3: Parameters of the absorption process affecting the Beer-Lambert law on UV-Vis spectroscopy.

Both factors can be summarized by expressing the absorbance  $A$  as a function of the concentration and of the cuvette length. In particular, the absorbance  $A$  is equal to the product of the extinction coefficient  $\epsilon$ , the concentration  $c$  and the path length  $l$

$$\text{Log} \left( \frac{I_0}{I} \right) = A = \epsilon \cdot l \cdot c \quad (\text{II})$$

Where:  $I_0$  is the intensity of the monochromatic light entering the sample and  $I$  is the intensity of the same light leaving the sample

$c$  is the sample concentration and is given in mol/L;

$l$ : The path length of the cuvette and is given in cm,

$\epsilon$  (Molar Absorption Coefficient) : is a sample specific constant describing how much the sample is absorbing at a given wavelength and is given in  $\text{L mol}^{-1} \text{ cm}^{-1}$ .

### III-Electronic Transitions [18-22]

According to molecular orbital theory, the excitation of a molecule by the absorption of radiation in the UV-visible regions involves promotion of its electrons from a bonding, or non-bonding (n) orbital to an antibonding orbital. There are  $\sigma$  and  $\pi$  bonding orbitals associated with  $\sigma^*$  and  $\pi^*$  antibonding orbitals, respectively. Non-bonding (n or p) orbitals are not associated with antibonding orbitals because non-bonding or lone pair of electrons present in them do not form bonds. A simplified energy diagram illustrating the transitions is shown in Figure 4

#### III.1- $\sigma \rightarrow \sigma^*$ transition

These transitions can occur in such compounds in which all the electrons are involved in single bonds. A typical example would be the single valence bond between two carbons atoms as found in saturated hydrocarbons.

#### III.2- $n \rightarrow \sigma^*$ transition

n-Electrons (lone pair) are nonbonding electrons found on atoms such as N, O, halogens, and S. Saturated compounds with lone pair of electrons undergo  $n \rightarrow \sigma^*$  transition in addition to  $\sigma \rightarrow \sigma^*$  transition.

Absorption, although at a longer wavelength than for saturated hydrocarbons, occurs below 200 nm. Ethers, thioethers, disulfides, alkyl halides, and alkyl amines have n-electrons and are classified as being transparent in the ultraviolet.

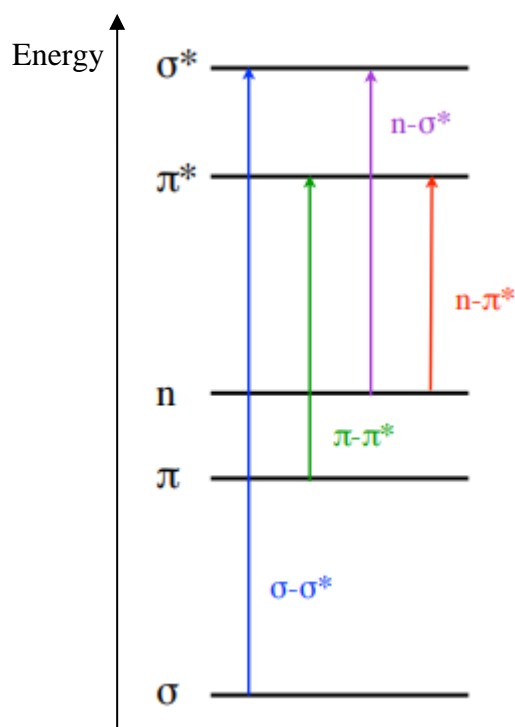


Figure 4: Energy level diagram of electronic transitions for an organic molecule.

### III.3- $\pi\rightarrow\pi^*$ transition

An unsaturated bond contains four electrons, two of which are  $\pi$ -electrons and two are  $\sigma$ -electrons. Of the types of electrons existing in the molecule, the  $\pi$ -electrons are the easiest to excite. Generally, the transition of a  $\pi$ -electron requires relatively higher amount of energy than  $n$ -electron and results in absorption in the ultraviolet or visible region. Typical examples are benzene, ethylene, and the carbonyl group. The  $>\text{C}=\text{O}$  group of saturated aldehydes or ketones exhibit an absorption of high intensity at about 180 nm.

### III.4- $n\rightarrow\pi^*$ transition

Compounds having double bonds between heteroatoms such as  $\text{C}=\text{O}$ ,  $\text{C}=\text{S}$ , and  $\text{N}=\text{O}$ , undergo  $n\rightarrow\pi^*$  transition. The  $>\text{C}=\text{O}$  group of saturated aldehydes or ketones exhibit an absorption of low intensity at about 285 nm.

## IV-Terms used in Spectroscopy UV-Visible

### IV.1- Chromophore

A covalently unsaturated group responsible for absorption in the UV or visible region is known as a chromophore. For example, C=C, C≡C, C=O, C=N, N=N, NO<sub>2</sub> etc. If a compound absorbs light in the visible region (400-800 nm), only then it appears colored. Thus, a chromophore may or may not impart color to a compound depending on whether the chromophore absorbs radiation in the visible or UV region.

Characteristics of some common unconjugated chromophores are given in Table 1

Table 1. Characteristics of some common unconjugated chromophores [23]

Chromophore	Example	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$	Transition	Solvent
C=C	Ethylene	171	15,530	$\pi \rightarrow \pi^*$	Vapor
C≡C	Acetylene	150	10,000	$\pi \rightarrow \pi^*$	Hexane
		173	6000	$\pi \rightarrow \pi^*$	Vapor
C=O	Acetaldehyde	160	20,000	$n \rightarrow \sigma^*$	Vapor
		180	10,000	$\pi \rightarrow \pi^*$	Vapor
		290	17	$n \rightarrow \pi^*$	Hexane
	Acetone	166	16,000	$n \rightarrow \sigma^*$	Vapor
		188	900	$\pi \rightarrow \pi^*$	Hexane
		279	15	$n \rightarrow \pi^*$	Hexane
-COOH	Acetic acid	204	60	$n \rightarrow \pi^*$	Water

### IV.2- Auxochrome

A covalently saturated group which, when attached to a chromophore, changes both the wavelength and the intensity of the absorption maximum is known as auxochrome, e.g. NH<sub>2</sub>, OH, SH, halogens etc. Auxochromes generally increase the value of  $\lambda_{\max}$  as well as  $\epsilon_{\max}$  by extending the conjugation through resonance. An auxochrome itself does not show absorption above 200 nm. Actually, the combination of chromophore and auxochrome behaves as a new chromophore having different values of  $\lambda_{\max}$  and  $\epsilon_{\max}$ . For example, benzene shows  $\lambda_{\max} = 256$  nm,  $\epsilon_{\max} = 200$ , whereas aniline shows  $\lambda_{\max} = 280$  nm,  $\epsilon_{\max} = 1430$  (both increased). Hence, NH<sub>2</sub> group is an auxochrome, which extends the conjugation

involving the lone pair of electrons on the nitrogen atom resulting in the increased values of  $\lambda_{\max}$  and  $\epsilon_{\max}$ .

### IV.3- Absorption and Intensity Shifts [21-22]

#### IV.3.1-Bathochromic shift.

The effect of an absorption maximum to a longer wavelength (Figure 5) due to the presence of an auxochrome, or solvent effect is called a bathochromic shift or red shift. For example, benzene shows  $\lambda_{\max}$  at 256 nm and aniline shows  $\lambda_{\max}$  at 280 nm. Thus, there is a bathochromic shift of 24 nm in the  $\lambda_{\max}$  of benzene due to the presence of the auxochrome  $\text{NH}_2$ .

Similarly, a bathochromic shift of  $n \rightarrow \pi^*$  band is observed in carbonyl compounds on decreasing solvent polarity, e.g.  $\lambda_{\max}$  of acetone is at 264.5 nm in water as compared to 279 nm in hexane.

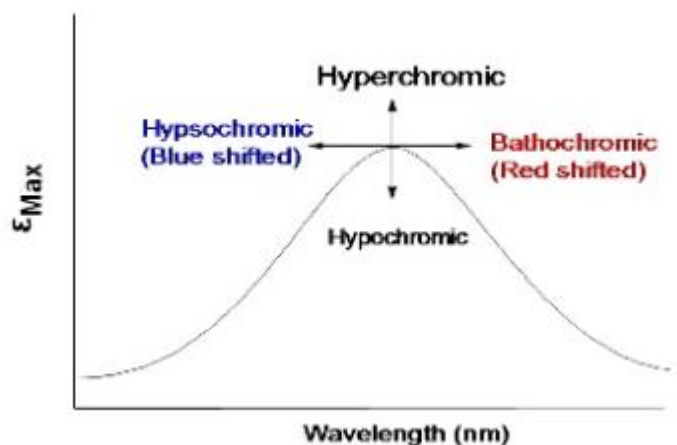


Figure 5: Absorption and intensity shifts

#### IV.3.2-Hypsochromic Shift

The shift of an absorption maximum to a shorter wavelength is called hypsochromic or blue shift (Figure 5). This is caused by the removal of conjugation or change in the solvent polarity. For example, aniline shows  $\lambda_{\max}$  at 280 nm, whereas anilinium ion (acidic solution of aniline) shows  $\lambda_{\max}$  at 254 nm. This hypsochromic shift is due to the removal of  $n - \pi$  conjugation of the lone pair of electrons of the nitrogen atom of aniline with the  $n$ -bonded

system of the benzene ring on protonation because the protonated aniline (anilinium ion) has no lone pair of electrons for conjugation.

Similarly, there is a hypochromic shift of 10-20 nm in the  $\lambda_{\max}$  of  $n \rightarrow n^*$  bands of carbonyl compounds on going from ethanol as solvent to hexane, i.e. on decreasing solvent polarity.

#### **IV.3.3-Hyperchromic Effect**

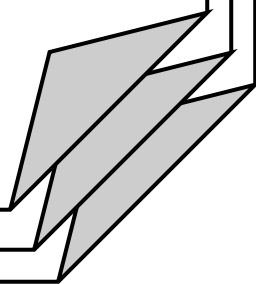
An effect, which leads to an increase in absorption intensity  $\lambda_{\max}$  is called hyperchromic effect (see Figure 5). The introduction of an auxochrome usually causes hyperchromic shift. For example, benzene shows B-band at 256 nm,  $\epsilon_{\max} = 200$ , whereas aniline shows B-band at 280 nm,  $\epsilon_{\max} 1430$ . The increase of 1230 in the value  $\epsilon_{\max}$  of aniline compared to that of benzene is due to the hyperchromic effect of the auxochrome  $\text{NH}_2$ .

#### **IV.3.4- Hypochromic Effect.**

An effect, which leads to a decrease in absorption intensity  $\epsilon_{\max}$ , is called hypochromic effect as shown in Figure 5. This is caused by the introduction of a group, which distorts the chromophore. For example, biphenyl shows  $\lambda_{\max}$  at 252 nm,  $\epsilon_{\max} 19000$ , whereas 2,2'-dimethylbiphenyl shows  $\lambda_{\max} = 270$  nm,  $\epsilon_{\max} = 800$ . The decrease of 18 200 in the value of  $\epsilon_{\max}$  of 2,2'-dimethylbiphenyl is due to the hypochromic effect of the methyl groups which distort the chromophore by forcing the rings out of coplanarity resulting in the loss of conjugation.

## **CHAPTER II**

### **Structural and electronic properties of Benzofuran-2-carboxylic acid derivatives**



## I-Introduction

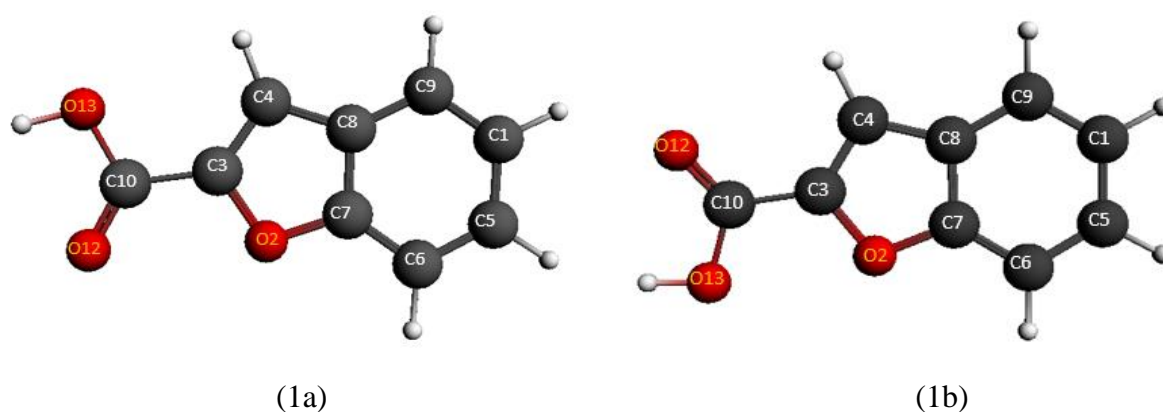
Molecular modeling covers a wide variety of theoretical and computational methods used to represent the structure of molecules [24]. It is essential as complements or for the interpretation and the comprehension of experimental work

In order to determine the substituent effects of benzofuran-2-carboxylic acid molecule substituted by OH, Cl, NH<sub>2</sub> and CH<sub>3</sub> at different position of the phenyl and furan rings. Theoretical calculations were performed in order to rationalize and identify their structural and electronic properties.

## II- Optimized geometry of benzofuran-2-carboxylic acid

Theoretical calculations for both benzo[b]furan-2-carboxylic acid (1a) and benzo[d]furan-2-carboxylic acid (1b) were performed in order to know the most stable structure. Optimized geometrical parameters of the most stable (1a) have been depicted and compared with experimental values (see Table 1).

From Table 1 the calculated bond lengths and bond angles are in good agreement with the experimental values. The obtained calculations are carried out in the gas phase whereas the experimental parameters are reported on the solid state.



**Figure 1.** Optimized geometry of benzofuran-2-carboxylic acid isomers (1a, 1b)

**Table 1.** Theoretical and experimental values of benzofuran-2-carboxylic acid

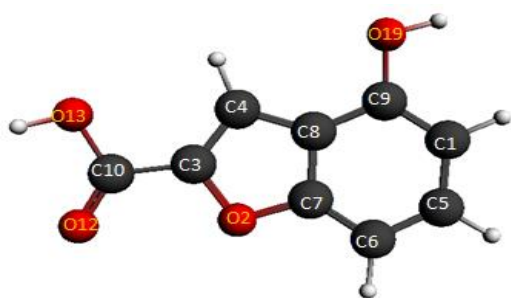
Bond lengths	Theor. Values	Exp. Values [25]
C1-C5	1,412	1,388
C5-C6	1,394	1,372
C6-C7	1,392	1,388
C7-C8	1,414	1,387
C8-C9	1,408	1,397
C9-C1	1,390	1,380
C8-C4	1,431	1,430
C4-C3	1,369	1,397
C3-C10	1,464	1,457
C10-O12	1,223	1,252
C10-O13	1,367	1,278
C3-O2	1,388	1,387
C7-O2	1,373	1,373
Angles		
C7-O2-C3	105,5	104,89
O2-C3-C10	119,5	116,87
O12-C10-O13	123,4	124,46
C10-C3-C4	128,7	131,25
O2-C7-C8	110,7	110,94
C7-C8-C9	118,9	119,01
O2-C7-C6	125,8	125,48
C1-C5-C6	121,6	122,36

### III-Structural properties of mono-substituted benzofuran-2-carboxylic acid

The interaction of benzofuran-2-carboxylic acid molecule with a substituent group is of great importance in determining its structural and electronic properties

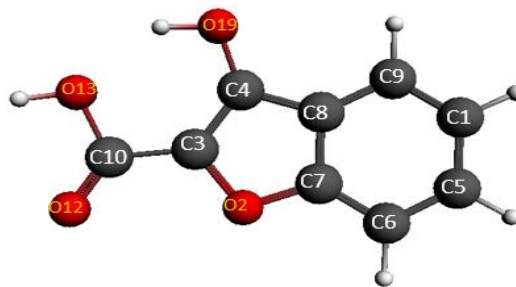
#### III.1-Geometries and stability of hydroxybenzofuran-2-carboxylic acid isomers

Optimized geometries of hydroxybenzofuran-2-carboxylic acid lead to different isomers depending on the position of the OH on phenyl and furan rings. The energetic and geometric parameters are gathered in Table 2. The lower energy structure corresponds to the compound 2a which have hydroxyl group on phenyl ring and far from the oxygen of furan ring. The results in Table 2 show that the introduction of OH acts slightly on the structural parameters of benzofuran-2-carboxylic and the variation in the bond lengths does not exceed 0.03 Å



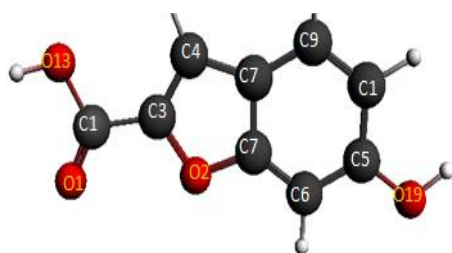
(2a)

Er = 00,00



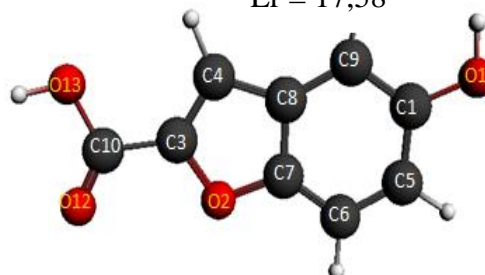
(2b)

Er = 17,58



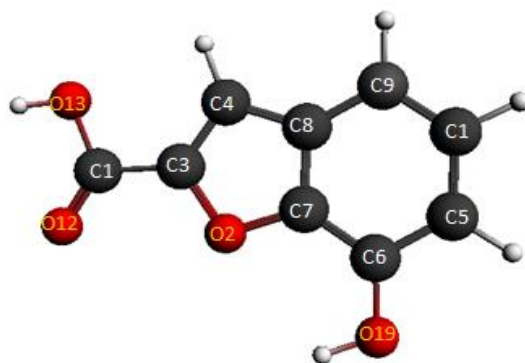
(2c)

Er = 19,50



(2d)

Er = 20,52



(2e)

Er = 21,93

**Figure 02.** Molecular structures and relative energy (kcal / mole) to the ground state energy of hydroxybenzofuran-2-carboxylic acid isomers.

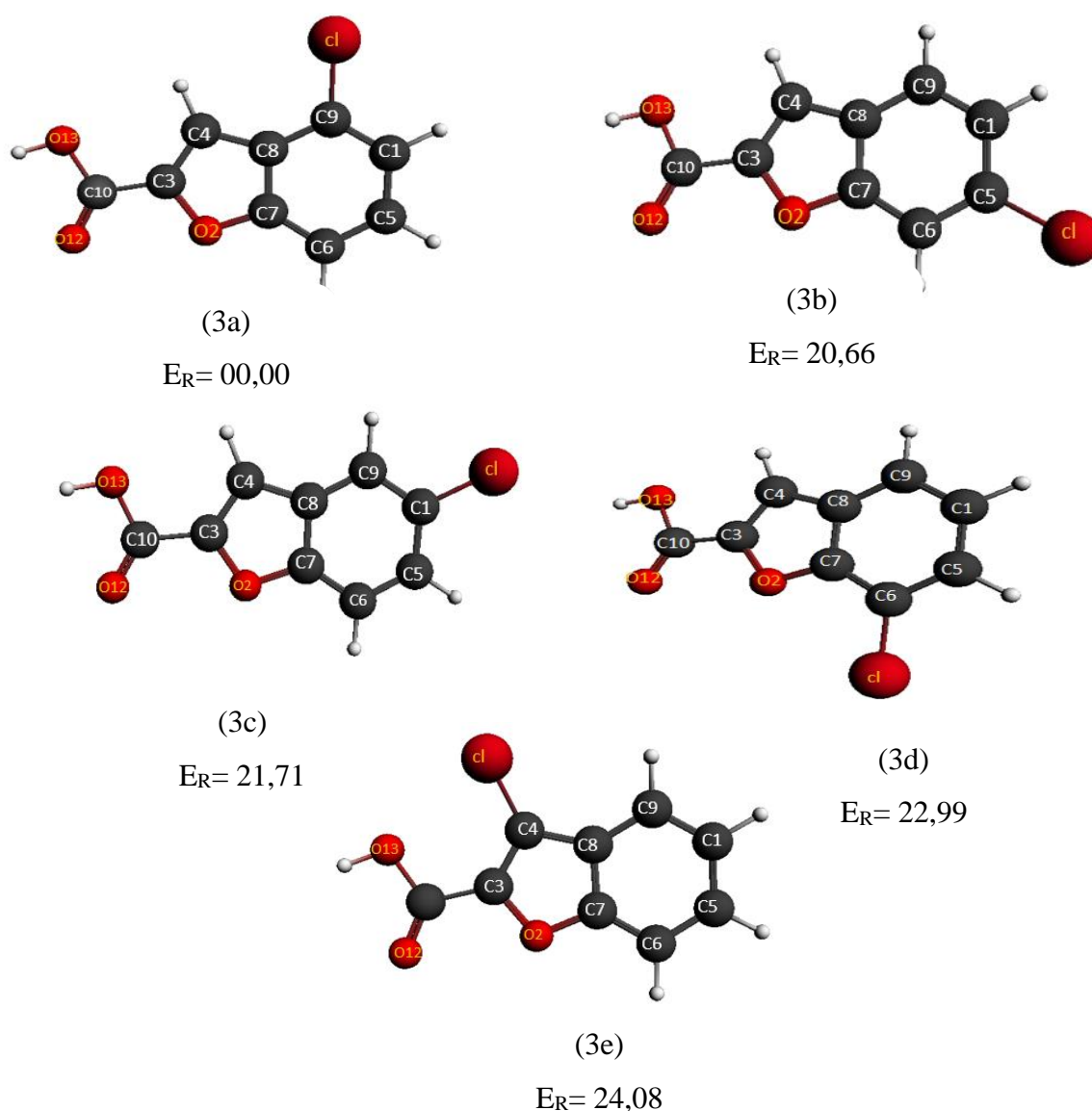
**Table 2.** Binding Energies (Kcal/ mol) and Selected optimized bond lengths (Å) and angles (°) of 2a-2e compounds

	2a	2b	2c	2d	2e
Binding Energy	-2939,07	-2921,49	-2919,57	-2918,55	-2917,14
Bond lengths					
C1-C5	1,410	1,410	1,431	1,422	1,405
C5-C6	1,394	1,396	1,407	1,389	1,410
C6-C7	1,393	1,393	1,387	1,391	1,419
C7-C8	1,412	1,411	1,413	1,409	1,409
C8-C9	1,410	1,400	1,405	1,412	1,404
C9-C1	1,393	1,390	1,391	1,410	1,389
C8-C4	1,428	1,438	1,432	1,438	1,430
C4-C3	1,371	1,397	1,367	1,371	1,363
C3-C10	1,463	1,451	1,471	1,478	1,478
C10-O12	1,219	1,205	1,208	1,207	1,207
C10-O13	1,377	1,385	1,354	1,353	1,354
C3-O2	1,385	1,400	1,391	1,378	1,392
C7-O2	1,371	1,371	1,376	1,383	1,394
C9-O19	1,374	/	/	/	/
C4-O19	/	1,322	/	/	/
C5-O19	/	/	1,341	/	/
C1-O19	/	/	/	1,345	/
C6-O19	/	/	/	/	1,336
O19-H	0,975	0,970	1,504	1,957	0,957
O13-H14	0,981	0,960	0,962	0,962	0,961
Angles (°)					
C7-O2-C3	106,0	105,5	105,7	105,4	105,2
O2-C3-C10	116,2	119,2	117,6	111,1	120,4
O12-C10-O13	123,1	123,6	125,0	125,0	125,2
C10-C3-C4	132,2	129,6	130,8	130,8	128,0
O2-C7-C8	110,1	111,5	110,5	111,1	110,4
C7-C8-C9	118,6	120,1	118,0	119,5	121,2
O2-C7-C6	125,8	126,1	125,2	126,2	127,0
C1-C5-C6	122,2	121,8	119,9	122,0	122,6
C8-C9-O19	117,6	/	/	/	/
C9-O19-H15	108,2	/	/	/	/
C3-C4-O19	/	129,4	/	/	/
C8-C4-O19	/	124,7	/	/	/
C6-C5-O19	/	/	117,8	/	/
C5-O19-C1	/	/	122,4	/	/
C5-C1-O19	/	/	/	116,2	/
C9-C1-O19	/	/	/	124,2	/
C5-C6-O19	/	/	/	/	119,3

### III.2-Geometries and stability of Chlorobenzofuran-2-carboxylic acid isomers

Optimized geometries of Chlorobenzofuran-2-carboxylic acid lead to different isomers depending on the position of the Cl on phenyl and furan rings. The geometric parameters are gathered in Table 3. The lower energy structure correspond to the compound 3a which have Cl atom on phenyl ring and far from the oxygen of furan ring.

Analyzing the results reported in the Table 3, we can clearly see that the introduction of Cl atom acts slightly on the structural parameters of benzofuran-2-carboxylic.



**Figure 03.** Molecular structures and relative energy (kcal / mole) to the ground state energy of Chlorobenzofuran-2-carboxylic acid isomers.

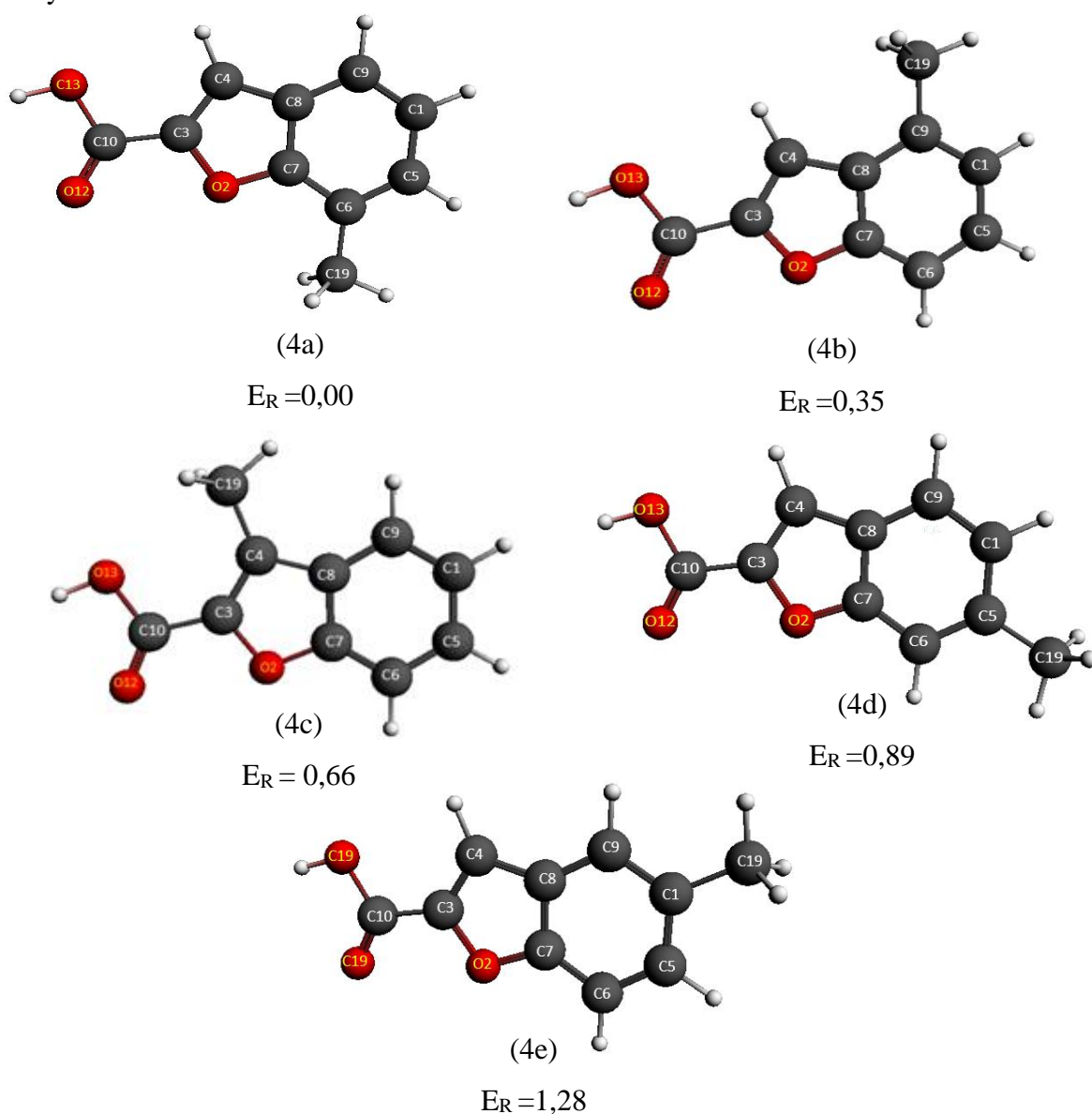
**Table 3.** Binding Energies (Kcal/ mol) and Selected optimized bond lengths (Å) and angles (°) of 3a-3e compounds

	3a	3b	3c	3d	3e
Binding Energy	-2750,16	-2729,50	-2729,45	-2727,17	-2726,08
Bond lengths					
C1-C5	1,411	1,421	1,421	1,409	1,410
C5-C6	1,394	1,407	1,396	1,409	1,395
C6-C7	1,370	1,394	1,391	1,408	1,393
C7-C8	1,414	1,411	1,410	1,413	1,408
C8-C9	1,406	1,404	1,407	1,403	1,402
C9-C1	1,388	1,388	1,400	1,388	1,392
C8-C4	1,428	1,430	1,433	1,430	1,446
C4-C3	1,371	1,366	1,367	1,364	1,389
C3-C10	1,467	1,476	1,478	1,475	1,470
C10-O12	1,218	1,207	1,207	1,206	1,209
C10-O13	1,375	1,352	1,350	1,351	1,349
C3-O2	1,384	1,390	1,383	1,386	1,390
C7-O2	1,370	1,381	1,382	1,377	1,372
C9-cl	1,753	/	/	/	/
C5-cl	/	1,726	/	/	/
C1-cl	/	/	1,731	/	/
C6-cl	/	/	/	1,714	/
C4-cl	/	/	/	/	1,698
O13-H14	0,981	0,962	0,962	0,962	0,963
Angles (°)					
C7-O2-C3	105,8	105,6	105,4	105,5	106,4
O2-C3-C10	116,0	118,9	118,5	118,5	115,2
O12-C10-O13	123,4	125,1	125,2	125,8	125,1
C10-C3-C4	132,2	129,5	129,6	129,3	133,8
O2-C7-C8	110,3	110,2	110,8	110,5	110,8
C7-C8-C9	117,9	118,5	120,2	120,7	119,3
O2-C7-C6	125,8	119,2	125,2	126,6	125,9
C6-C5-C1	122,1	120,5	121,8	122,2	121,4
C8-C9-cl	119,7	/	/	/	/
C1-C9-cl	120,6	/	/	/	/
C1-C5-cl	/	119,2	/	/	/
C6-C5-cl	/	120,4	/	/	/
C5-C1-cl	/	/	119,4	/	/
C9-C1-cl	/	/	120,5	/	/
C5-C6-cl	/	/	/	122,4	/
C7-C6-cl	/	/	/	122,4	/
C3-C4-cl	/	/	/	/	129,4
C8-C4-cl	/	/	/	/	124,6

### III.3-Geometries and stability of methylbenzofuran-2-carboxylic acid isomers

Optimized geometries of methylbenzofuran-2-carboxylic acid lead to different isomers depending on the position of the CH<sub>3</sub> on phenyl and furan rings. The geometric parameters are gathered in Table 4. Five energetically close structures are found (have almost identical total energy). The lower energy structure correspond to the compound 4a which have CH<sub>3</sub> atom on phenyl ring and near the oxygen of furan ring.

Analyzing the results reported in the table 3, we can clearly see that the introduction of Cl atom acts slightly on the structural parameters of benzofuran-2-carboxylic.



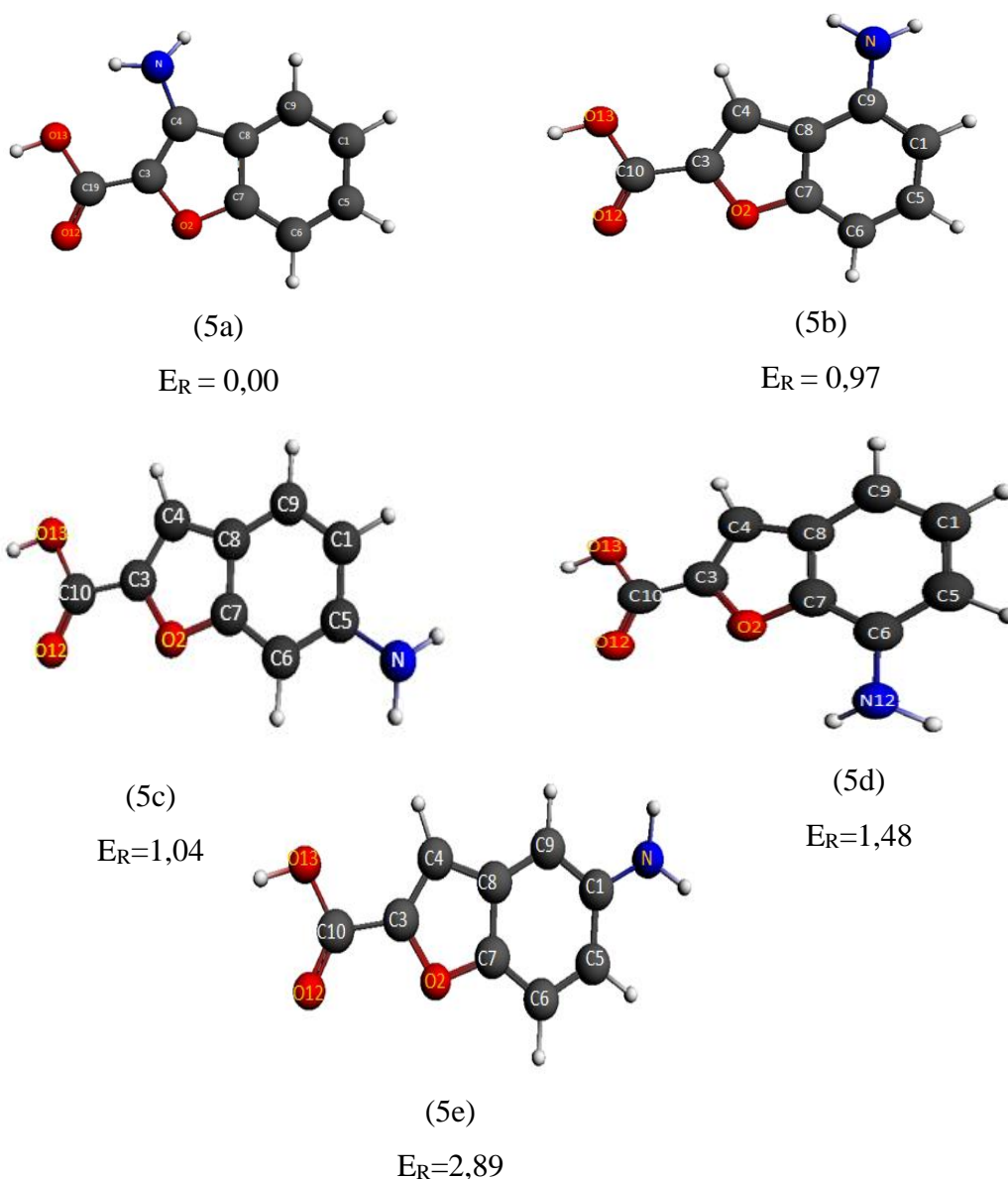
**Figure 04.** Molecular structures and relative energy (kcal / mole) to the ground state energy of Chlorobenzofuran-2-carboxylic acid isomers.

**Table 4.** Binding Energies (Kcal/ mol) and Selected optimized bond lengths (Å) and angles (°) of 4a-4e compounds

	4a	4b	4c	4d	4e
Binding Energy	-3166,10	-3165,75	-3165,44	-3165,21	-3164,82
bond lengths (Å)					
C1-C5	1,412	1,412	1,412	1,421	1,420
C5-C6	1,398	1,393	1,394	1,397	1,392
C6-C7	1,399	1,392	1,392	1,392	1,392
C7-C8	1,412	1,412	1,410	1,411	1,411
C8-C9	1,408	1,415	1,408	1,409	1,409
C9-C1	1,389	1,394	1,390	1,387	1,393
C8-C4	1,431	1,432	1,439	1,430	1,431
C4-C3	1,371	1,372	1,380	1,372	1,372
C3-C10	1,464	1,464	1,462	1,463	1,464
C10-O12	1,219	1,219	1,220	1,219	1,219
C10-O13	1,378	1,378	1,380	1,378	1,378
C3-O2	1,383	1,383	1,389	1,385	1,383
C7-O2	1,374	1,372	1,367	1,371	1,372
C6-C19	1,504	/	/	/	/
C9-C19	/	1,505	/	/	/
C4-C19	/	/	1,497	/	/
C5-C19	/	/	/	1,509	/
C1-C19	/	/	/	/	1,511
O13-H14	0,981	0,981	0,981	0,981	0,981
Angles (°)					
C7-O2-C3	105,7	105,7	105,7	105,6	105,5
O2-C3-C10	116,1	116,2	114,6	116,1	116,0
O12-C10-O13	123,0	123,0	122,5	123,0	123,0
C10-C3-C4	132,2	132,1	133,3	132,2	132,2
O2-C7-C8	110,7	110,7	110,6	110,7	110,9
C7-C8-C9	119,9	119,9	119,0	118,4	119,1
O2-C7-C6	124,7	125,6	125,8	125,5	126,0
C1-C5-C6	122,7	121,8	121,6	119,7	122,7
C5-C6-C19	123,6	/	/	/	/
C1-C6-C19	/	/	/	/	/
C1-C9-C19	/	122,4	/	/	/
C8-C9-C19	/	/	/	/	/
C8-C4-C19	/	/	126,0	/	/
C3-C4-C19	/	/	128,7	/	/
C6-C5-C19	/	/	/	120,7	/
C1-C5-C19	/	/	/	122,7	/
C9-C1-C19	/	/	/	/	121,0
C5-C1-C19	/	/	/	/	119,5

## III.4-Geometries and stability of aminobenzofuran-2-carboxylic acid isomers

Optimized geometries of aminobenzofuran-2-carboxylic acid lead to different isomers depending on the position of the NH<sub>2</sub> on phenyl and furan rings. The energetic and geometric parameters are gathered in Table 5. The five structures have almost identical total energy. The lower energy structure corresponds to the compound 5a which have amino group on furan ring. The results in Table 5 show that the introduction of NH<sub>2</sub> acts slightly on the structural parameters of benzofuran-2-carboxylic and the variation in the bond lengths does not exceed 0.03 Å



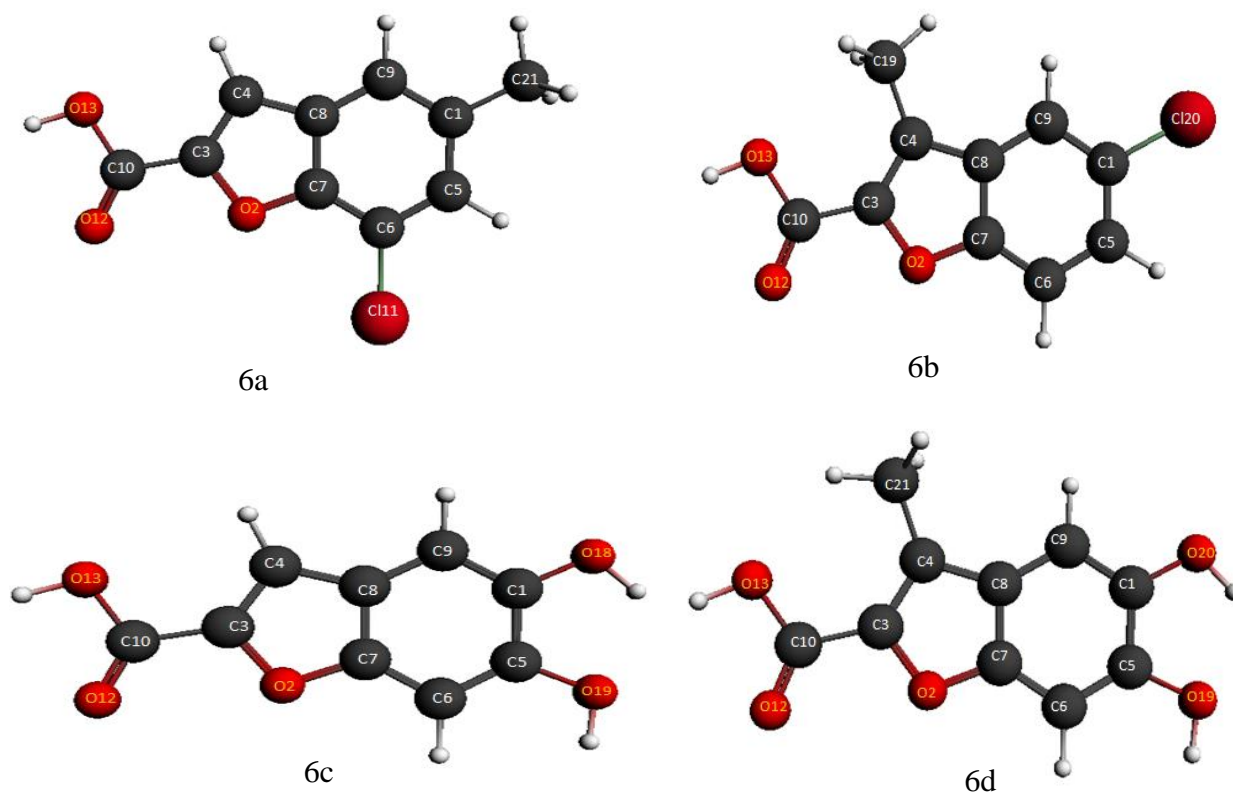
**Figure 05.** Molecular structures and relative energy (kcal / mole) to the ground state energy of aminobenzofuran-2-carboxylic acid isomers.

**Table 5.** Binding Energies (Kcal/ mol) and Selected optimized bond lengths (Å) and angles (°) of 2a-2e compounds

	5a	5b	5c	5d	5e
Binding Energy	-3064,23	-3063,26	-3063,19	-3062,75	-3061,34
Bond lengths (Å)					
C1-C5	1,411	1,407	1,423	1,410	1,421
C5-C6	1,394	1,395	1,402	1,402	1,391
C6-C7	1,393	1,392	1,388	1,402	1,392
C7-C8	1,410	1,412	1,414	1,407	1,411
C8-C9	1,405	1,417	1,408	1,410	1,407
C9-C1	1,391	1,399	1,385	1,390	1,396
C8-C4	1,441	1,429	1,428	1,433	1,407
C4-C3	1,389	1,372	1,372	1,372	1,373
C3-C10	1,443	1,461	1,458	1,463	1,463
C10-O12	1,221	1,219	1,221	1,220	1,219
C10-O13	1,397	1,380	1,320	1,377	1,378
C3-O2	1,398	1,383	1,390	1,384	1,381
C7-O2	1,365	1,373	1,369	1,374	1,374
C4-N	1,379	/	/	/	/
C9-N	/	1,398	/	/	/
C5-N	/	/	1,400	/	/
C6-N	/	/	/	1,396	/
C1-N	/	/	/	/	1,410
O13-H14	0,981	0,981	0,981	0,981	0,981
Angles (°)					
C7-O2-C3	105,7	106,0	105,7	105,3	105,4
O2-C3-C10	116,5	116,4	116,2	115,9	116,1
O12-C10-O13	121,7	122,9	122,7	123,0	122,9
C10-C3-C4	132,2	132,1	132,2	132,5	132,1
O2-C7-C8	111,4	110,3	110,7	111,3	111,0
C7-C8-C9	119,5	119,4	118,2	119,4	119,5
O2-C7-C6	125,6	125,6	125,2	124,2	126,2
C1-C5-C6	121,6	122,4	120,2	122,0	122,2
C3-C4-N	128,2	/	/	/	/
C8-C4-N	125,8	/	/	/	/
C1-C9-N	/	122,2	/	/	/
C8-C9-N	/	120,7	/	/	/
C1-C5-N	/	/	119,3	/	/
C6-C5-N	/	/	120,41	/	/
C5-C6-N	/	/	/	123,9	/
C7-C6-N	/	/	/	121,3	/
C9-C1-N	/	/	/	/	121,0

**IV-Structural properties of di and tri-substituted benzofuran-2-carboxylic acid**

The optimized geometries of di and tri-substituted benzofuran-2-carboxylic acid are depicted in Figure 6. Structural parameters including bond lengths and angle of the molecules are listed in Table 6. Analyzing the results reported in the table 6, we can clearly see that that the introduction of two or three groups acts slightly on the structural parameters of benzofuran-2-carboxylic.



**Figure 6.** Optimized geometry of compounds 6a, 6b, 6c, 6d

**Table 6.** Binding Energies (Kcal/ mol) and Selected bond lengths (Å) and Angles (°) for 6a, 6b, 6c, 6d structures

Distance	6a	6b	6c	6d
Binding energies	-3124,87	-3127,21	-3088,8	-3466,57
bond lengths (Å)				
C1-C5	1,418	1,410	1,424	1,423
C5-C6	1,391	1,393	1,390	1,390
C6-C7	1,395	1,392	1,394	1,394
C7-C8	1,411	1,409	1,411	1,406
C8-C9	1,407	1,407	1,409	1,409
C9-C1	1,392	1,388	1,385	1,386
C8-C4	1,432	1,439	1,429	1,438
C4-C3	1,371	1,380	1,373	1,382
C3-C10	1,466	1,464	1,461	1,461
C10-O12	1,218	1,219	1,220	1,221
C10-O13	1,377	1,379	1,379	1,381
C3-O2	1,348	1,388	1,387	1,394
C7-O2	1,366	1,366	1,369	1,365
C1-C19	1,510	/	/	/
C4-C19	/	1,497	/	/
C6-Cl11	1,745	/	/	/
C1-Cl20	/	1,761	/	/
C5-O19	/	/	1,384	1,384
C1-O18	/	/	1,374	/
C4-C21	/	/	/	1,495
C1-O20	/	/	/	1,375
Angles (°)				
C7-O2-C3	105,5	105,6	105,6	105,5
O2-C3-C10	119,5	116,0	116,0	116,1
O12-C10-O13	123,4	123,1	123,1	122,9
C10-C3-C4	128,7	132,1	132,1	132,4
O2-C7-C8	110,7	110,7	110,7	111,1
C7-C8-C9	118,9	119,0	119,0	119,4
O2-C7-C6	125,8	125,7	125,7	125,5
C1-C5-C6	121,6	121,6	121,6	122,1
H14-O13-C10	/	104,2	104,2	104,1
C5-C1-C19	/	119,1	/	/
C7-C6-Cl11	/	121,4	/	/
C5-C1-Cl20	/	/	121,6	/
C3-C4-C19	/	/	125,3	/
H18-C19-H21	/	109,5	109,5	/
C5-C1-O18	/	/	/	119,3
C9-C1-O18	/	/	/	120,0
C1-C5-O19	/	/	/	114,1
C1-O18-H17	/	/	/	107,0
C5-O19-H16	/	/	/	109,3
C6-C5-O19	/	/	/	123,8

### V-HOMO-LUMO energy gaps

The HOMO-LUMO gap is among the useful parameters evaluating the stability and chemical reaction of the organic compounds. A system with a large energy gap is chemically less reactive, therefore, could be more stable. In addition they play an important role in the determination of the UV-visible spectra. The calculated HOMO and LUMO energies are presented in Figure . It is interesting to mention that the calculated HOMO-LUMO gaps for all are in the range 3.24-2,58 eV (Figure 7), suggesting a good kinetic stability of the of Benzofuran-2-carboxylic acid derivatives

The largest HOMO-LUMO gap of 3.24 and 3.23 eV corresponds to 1a and 4e respectively , indicating that these compounds are the less reactive system and relatively the most stable.

The OH, Cl and NH<sub>2</sub> groups destabilize the energies of the HOMO and LUMO of Benzofuran-2-carboxylic acid. And as result the HOMO-LUMO gap decreased almost for all compound (see figure ).

As schown in figure 7 , the HOMO-LUMO gap decreased slighly for the methylbenzofuran-2-carboxylic acid isomers from 3,24 eV of 1a to 3,16 ; 3,11; 3,17; 2,57 and 3, 23 eV of 4a, 4b, 4c, 4d and 4e respectively.

### VI-Hirshfeld Charges Analysis

The influence of the addition of CH<sub>3</sub>, OH, NH<sub>2</sub> and Cl on Benzofuran-2-carboxylic acid, can be further explained from the Hirschfeld Charge analysis [26]. Hirschfeld charge calculations are widely applied in quantum chemical calculations because the atomic charges affect the electronic structure and dipole .To examine the electronic structure of Benzofuran-2-carboxylic acid derivatives, calculated charge distribution based on Hirschfeld population analysis are indicated in Table 7 and Tables A1, A2, A3, A4

All results show greatest negative charges on oxygen atoms of carboxylic function for each compounds

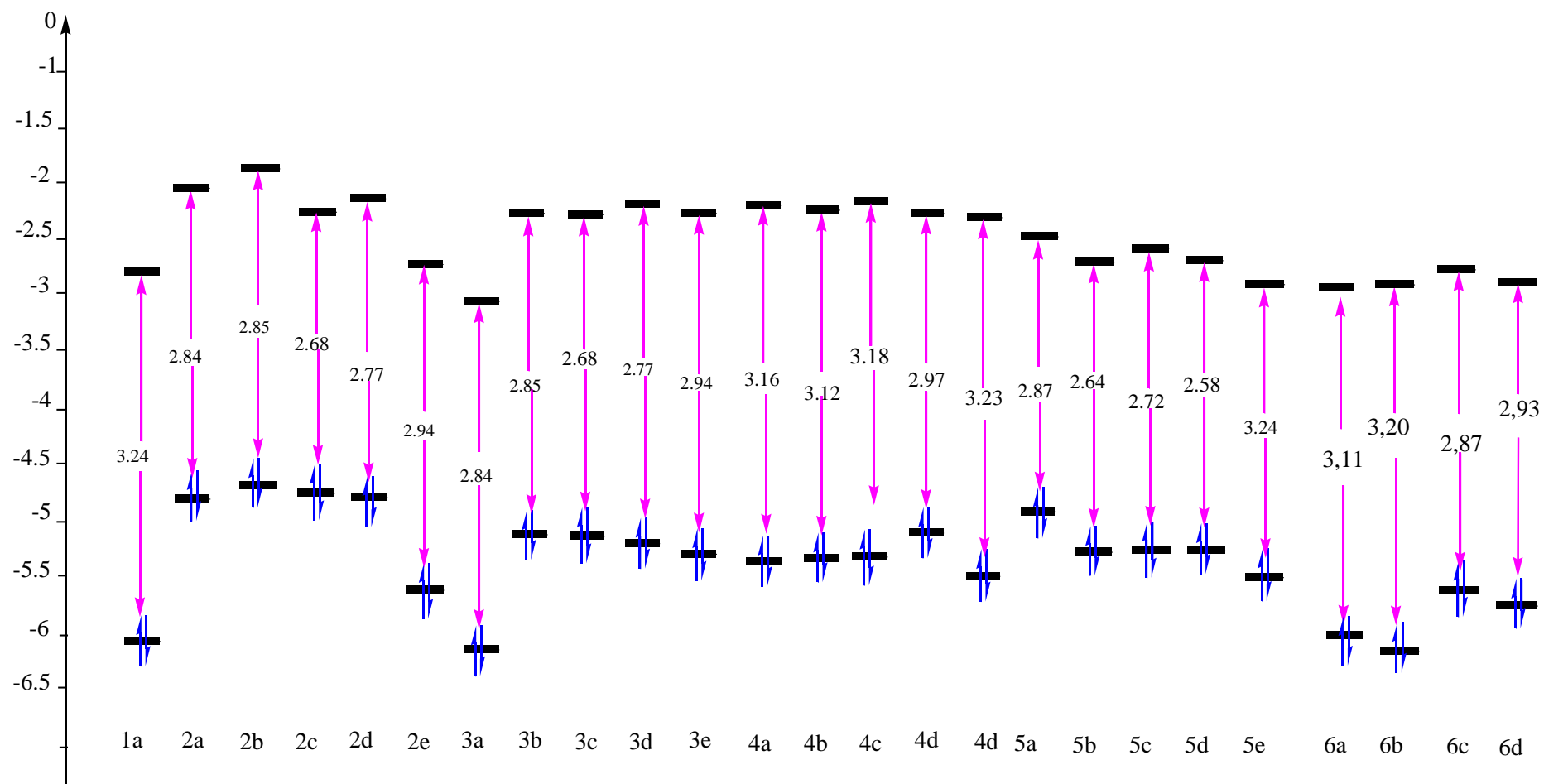


Figure 7: The HOMO and LUMO energies of Benzofuran-2-carboxylic acid derivatives

The dipole moment of all compound have been calculated and gathered in table 7 and Tables A1, A2, A3, A4. The Benzofuran-2-carboxylic acid (1a) possesses a low dipole moment value estimated at 2,73 debye. The substitution with NH<sub>2</sub> gives the highest dipole moment value of 4, 25 Debye.

**Table 7.** Hirshfeld charges and dipole moments (Debye) of Benzofuran-2-carboxylic acid (1a) and OH, Cl, CH<sub>3</sub> and NH<sub>2</sub> substituted on Benzofuran-2-carboxylic acid (2a, 3a, 4a, 5a, 6a, 6b, 6c and 6d)

	1a	2a	3a	4a	5a	6a	6b	6c	6d
C1	-0,050	-0,077	-0,058	-0,053	-0,052	0,008	0,012	0,051	0,053
C5	-0,039	-0,041	-0,036	-0,043	-0,040	-0,050	-0,048	0,062	0,059
C6	-0,047	-0,062	-0,047	0,008	-0,046	0,009	-0,042	-0,065	-0,074
C7	0,077	0,078	0,080	0,076	0,077	0,064	0,074	0,068	0,064
C8	-0,015	-0,031	-0,027	-0,019	-0,026	-0,017	-0,017	-0,027	-0,031
C9	-0,038	0,078	0,021	-0,046	-0,042	-0,047	-0,049	-0,060	-0,060
C4	-0,048	-0,051	-0,052	-0,054	0,043	-0,053	0,006	-0,057	0,002
C3	0,046	0,044	0,051	0,045	0,016	0,050	0,043	0,042	0,035
C10	0,171	0,169	0,172	0,169	0,157	0,172	0,170	0,167	0,165
O2	-0,068	-0,061	-0,057	-0,057	-0,074	-0,057	-0,064	-0,064	-0,072
O12	-0,263	-0,256	-0,251	-0,256	-0,266	-0,249	-0,255	-0,257	-0,262
O13	-0,161	-0,168	-0,164	-0,169	-0,168	-0,167	-0,156	-0,171	-0,160
O19/ Cl/N		-0,166	0,026	-0,104	-1,169	-0,019	-0,045	-0,165	-0,164
C19						-0,106	-0,105		
C21						/			-0,108
$\mu$		3,910	1,493	2,263	4,033	4,14	1,98	2,48	2,15

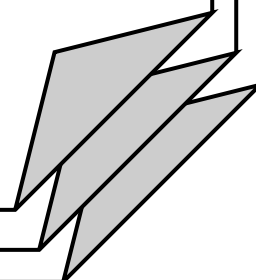
## **VII-Conclusion**

Since Benzofuran-2-carboxylic acid were widely used as starting compounds in the synthesis of pharmaceuticals , a comprehensive investigation on Benzofuran-2-carboxylic acid derivatives containing different substituents (Cl, NH<sub>2</sub>, OH and CH<sub>3</sub>) at different position of the phenyl or Furan ring has been performed.

It was found that the substituents effect (NH<sub>2</sub>, OH, CH<sub>3</sub>, Cl ) on the Benzofuran-2-carboxylic acid not cause significant changes in the optimized structures of the bonds and angles. The OH, Cl and NH<sub>2</sub> groups destabilize the energies of the HOMO and LUMO of Benzofuran-2-carboxylic acid and as result the HOMO-LUMO gap decreased from 3,24 eV of Benzofuran-2-carboxylic acid to about 2,58 eV as small value in Benzofuran-2-carboxylic acid substituted

# **CHAPTER III**

## **Electronic spectra of Benzofuran-2-carboxylic acid derivatives**



## I-Introduction

In order to understanding the theoretical UV–Vis spectra, TD-DFT calculations on the benzofuran-2 carboxylic acid molecule and their derivative -mono, di and tri-substituted at different position of benzene hydrogen or furan hydrogen by OH, NH<sub>2</sub>, Cl and CH<sub>3</sub>- in their optimized geometries (studied in Chapter II) allow indexing of absorption spectrum bands.

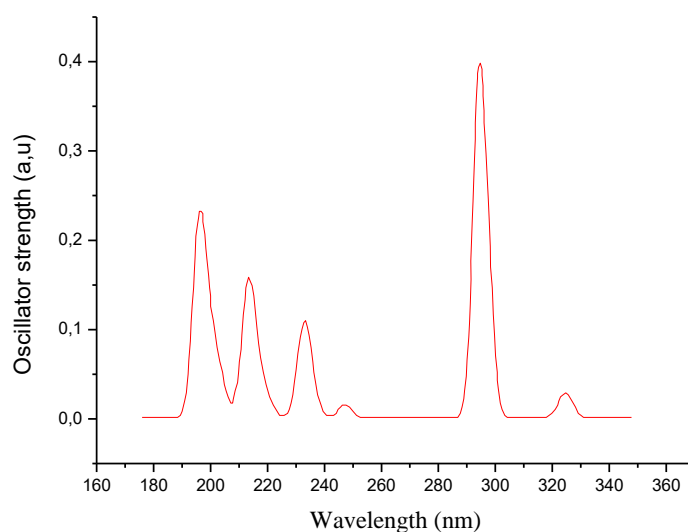
The principal electronic transitions, wavelengths, oscillator strengths and energies for 1a -5a , 6a-6d, 2b, 4c, 3e compounds are given in Tables 1- 6 and Table 5A, also theoretical electronic spectra and diagrams of electronic transitions are sketched. It is noticeable that only transitions with oscillator strengths larger than 0.01 are listed

## II-Spectroscopic Properties - UV-Visible spectra

### II.1-Electronic spectra of benzofuran-2-carboxylic acid (1a)

The theoretical electronic spectra (Figure 1) of the compound 1a obtained in gas phase shows six absorption bands appears in the ultraviolet region of 190-330 nm.

The first broadest band centered at 324 nm corresponds to the ( $n$  C-O of furan +  $\pi$  C-C of benzene  $\rightarrow \pi^*$  C-C +  $\pi^*$  C-O) electronic transitions assigned to HOMO-6 $\rightarrow$ LUMO (47,2%), HOMO-1 $\rightarrow$ LUMO+2 (18,0%) and HOMO-1 $\rightarrow$ LUMO+1 (10,5%) transitions with an oscillator strength 0,0290 (u.a)

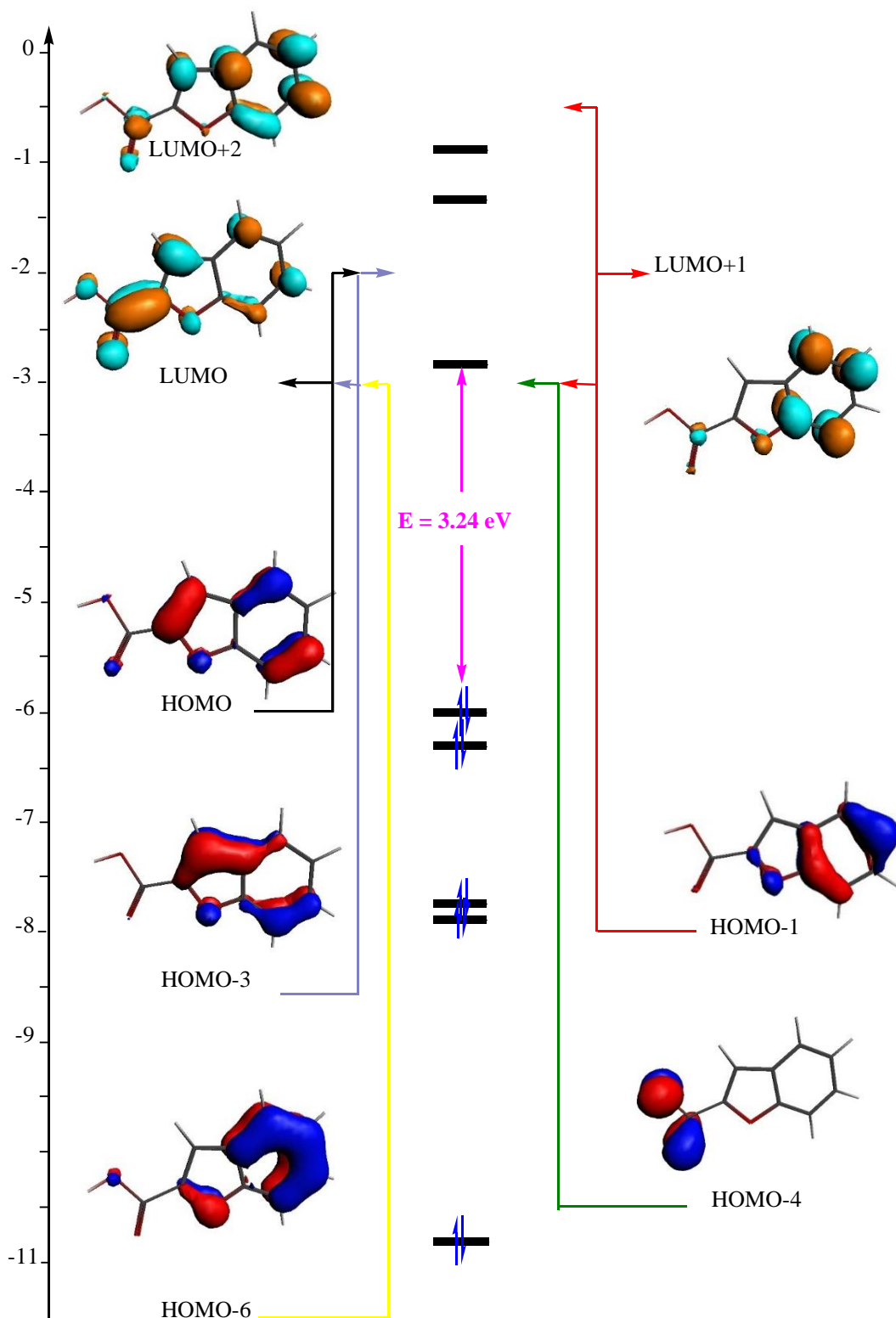


**Figure 1.** Theoretical electronic spectra for benzofuran-2-carboxylic acid (1a)

**Table 1.** Calculated electronic transitions and their assignments, the dominant contributions to electron excitations in percentages (%), wavelengths  $\lambda$  (nm), oscillator strengths  $f$  (au), and excitation energies (eV) of the compound 1a.

Excitation energies	$\lambda$ (nm)	Oscillator strengths	Electronic transition	Composition	Assignments
3,83	324	0,2294	HOMO-6 $\rightarrow$ LUMO HOMO-1 $\rightarrow$ LUMO+2 HOMO-1 $\rightarrow$ LUMO+1	47,2% 18,0% 10,5%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
4,13	300	0,0571	HOMO-1 $\rightarrow$ LUMO+2 HOMO $\rightarrow$ LUMO+2 HOMO-3 $\rightarrow$ LUMO+1 HOMO-3 $\rightarrow$ LUMO	32,8% 28,6% 13,8% 10,1%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
4,19	296	0,1540	HOMO-1 $\rightarrow$ LUMO+1 HOMO-3 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+1	36,4% 23,1% 17,0%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
5,01	247	0,0256	HOMO-4 $\rightarrow$ LUMO	84,4%	$n \rightarrow \pi^*$
5,51	225	0,1087	HOMO $\rightarrow$ LUMO+2 HOMO-1 $\rightarrow$ LUMO+1 HOMO-3 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+1 HOMO-1 $\rightarrow$ LUMO+2	30,2% 19,7% 18,2% 16,1% 10,0%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
5,65	219	0,0152	HOMO $\rightarrow$ LUMO+1 HOMO-3 $\rightarrow$ LUMO	50,9% 33,6%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
5,80	214	0,3988	HOMO $\rightarrow$ LUMO HOMO-1 $\rightarrow$ LUMO	52,3% 37,6%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
6,30	198	0,0290	HOMO-1 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO	53,8% 38,9%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$

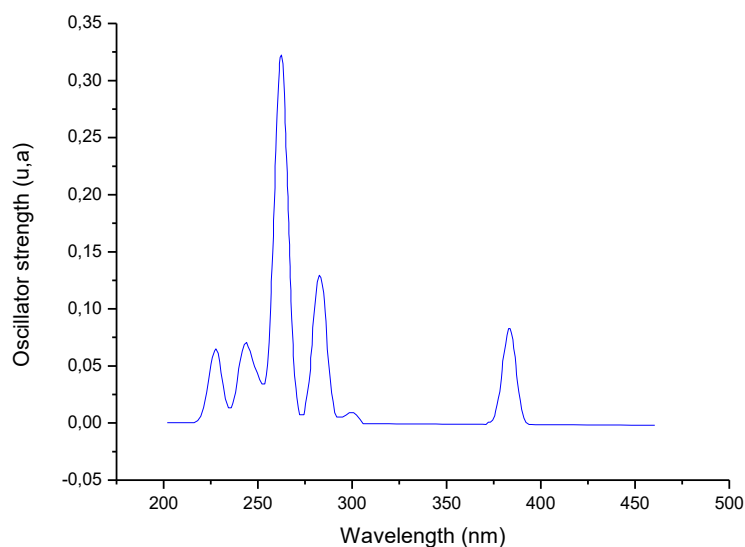
The second important band in the region of 280-310 nm due to the ( $n$  C-O of furan +  $\pi$  C-C of benzene  $\rightarrow \pi^*$  C-C +  $\pi^*$  C-O) transitions corresponding to the HOMO-1 $\rightarrow$ LUMO+1 (36,4%), HOMO-3 $\rightarrow$ LUMO (23,1%) and HOMO  $\rightarrow$  LUMO+1 (17,0%) electronic transitions with an oscillator strength of 0,1540 (u.a).



**Figure 2.** Diagram of electronic transitions of the benzofuran-2-carboxylic acid (1a)

## II.2-Electronic spectra of 4-hydroxybenzofuran-2-carboxylic acid (2a)

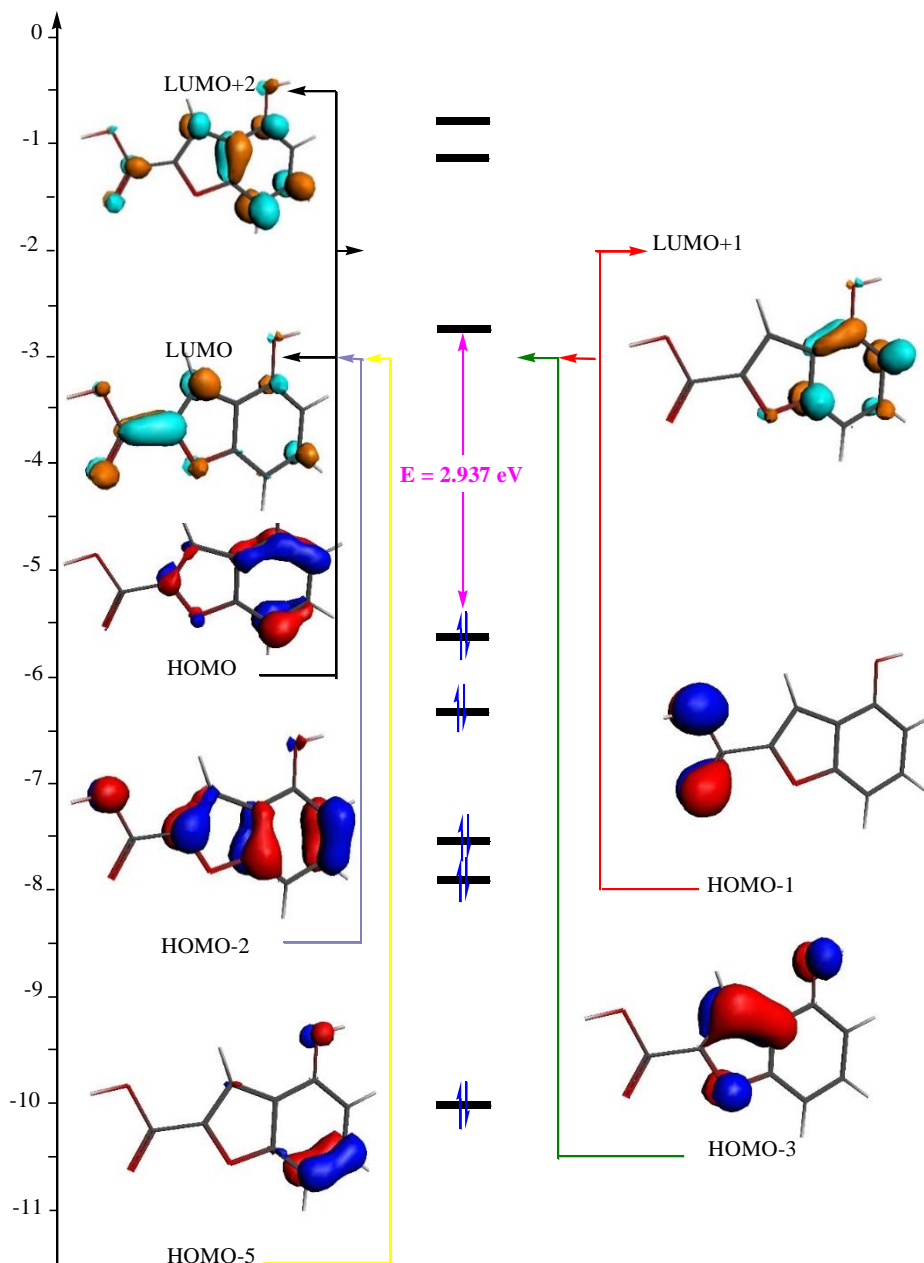
For the 2a compound spectra (figure 3), the first broadest band appears essentially in the ultraviolet region centered at 384 (nm) corresponding to the intense ( $n$  (Cl and C-O of furan)  $+\pi$  C-C of benzene  $\rightarrow\pi^*$ ) transitions. This transition corresponding to excitation from HOMO $\rightarrow$ LUMO (88,1%) which is shifted by about 60 (nm) than that to the compound 1a.



**Figure 3.** Theoretical electronic spectra for 4-hydroxybenzofuran-2-carboxylic acid (2a)

**Table 2.** Calculated electronic transitions and their assignments of the compound 2a.

Excitation energies	$\lambda$ (nm)	Oscillator strengths	Electronique transition	Composition	assignments
5,45	227	0,0646	HOMO-3 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+2 HOMO-5 $\rightarrow$ LUMO	33,6 % 24,7 % 14,9 %	$n+\pi \rightarrow\pi^*$ $n+\pi \rightarrow\pi^*$ $n+\pi \rightarrow\pi^*$
5,11	243	0,0628	HOMO-3 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+2 HOMO $\rightarrow$ LUMO+1	38,7 % 27,3 % 11,0 %	$n+\pi \rightarrow\pi^*$ $n+\pi \rightarrow\pi^*$ $n+\pi \rightarrow\pi^*$
4,97	249	0,0334	HOMO-1 $\rightarrow$ LUMO+1	89,8 %	$n \rightarrow\pi^*$
4,73	262	0,3234	HOMO-2 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+1 HOMO $\rightarrow$ LUMO+2	30,7 % 29,8 % 23,4 %	$n+\pi \rightarrow\pi^*$ $n+\pi \rightarrow\pi^*$ $n+\pi \rightarrow\pi^*$
4,38	283	0,1308	HOMO-2 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+1	41,2 % 39,4 %	$n+\pi \rightarrow\pi^*$ $n+\pi \rightarrow\pi^*$
4.14	299	0,0107	HOMO-1 $\rightarrow$ LUMO HOMO-2 $\rightarrow$ LUMO	80,9 % 11,3 %	$n\rightarrow\pi^*$ $n+\pi \rightarrow\pi^*$
3,23	384	0,0834	HOMO $\rightarrow$ LUMO	88,1 %	$n+\pi \rightarrow\pi^*$



**Figure 4.** Diagram of electronic transitions of the 4-hydroxybenzofuran-2-carboxylic acid (2a)

### II.3-Electronic spectra of 4-Chlorobenzofuran-2-carboxylic acid (3a)

In the electronic spectrum of compound 3a (Figure 5), the absorption bands are in the ultraviolet region of 235-385 nm. The first band found low energy centered at 385 nm corresponds to the  $(n(\text{Cl and C-O of furan}) \rightarrow \pi^* \text{ C-C} + \pi^* \text{ C-O})$  electronic transition assigned to HOMO-2 $\rightarrow$ LUMO (91,4%) transition.

The second absorption band centered at 297 nm corresponding to the intense ( $n \text{ C=O}, \text{OH} \rightarrow \pi^* \text{ C-C} + \pi^* \text{ C-O}$ ) transition. This transition corresponding to excitation from HOMO-2 (which is made of carboxylic acid) to LUMO (which is made of benzofuran). (91,4%).

The two electronic spectra of 3a and 2a, exhibit similar shapes but with somewhat differences concerning the bands positions and their widths.

**Table 3.** Calculated electronic transitions and their assignments of the compound 3a.

Excitation energies	$\lambda$ (nm)	Oscillator strengths	Electronic transition	Composition	Assignments
3,22	385	0,03	HOMO $\rightarrow$ LUMO	90,4%	$n+\pi \rightarrow \pi^*$
4,18	297	0,008	HOMO-2 $\rightarrow$ LUMO	91,4%	$n \rightarrow \pi^*$
4,31	288	0,11	HOMO-1 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+1 HOMO $\rightarrow$ LUMO+2	47,3% 26,0% 15,1%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
4,74	262	0,44	HOMO-1 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+1	41,3% 36,3%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
4,78	259	0,039	HOMO-3 $\rightarrow$ LUMO HOMO-1 $\rightarrow$ LUMO+2 HOMO $\rightarrow$ LUMO+1	70,0% 13,8% 11,3%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
4,96	250	0,045	HOMO-2 $\rightarrow$ LUMO+1 HOMO $\rightarrow$ LUMO+2	55,0% 27,5%	$n \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
5,01	247	0,08	HOMO $\rightarrow$ LUMO+2 HOMO-2 $\rightarrow$ LUMO+1	43,1% 34,3%	$n+\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
5,28	235	0,024	HOMO-1 $\rightarrow$ LUMO+1	73,7%	$n+\pi \rightarrow \pi^*$

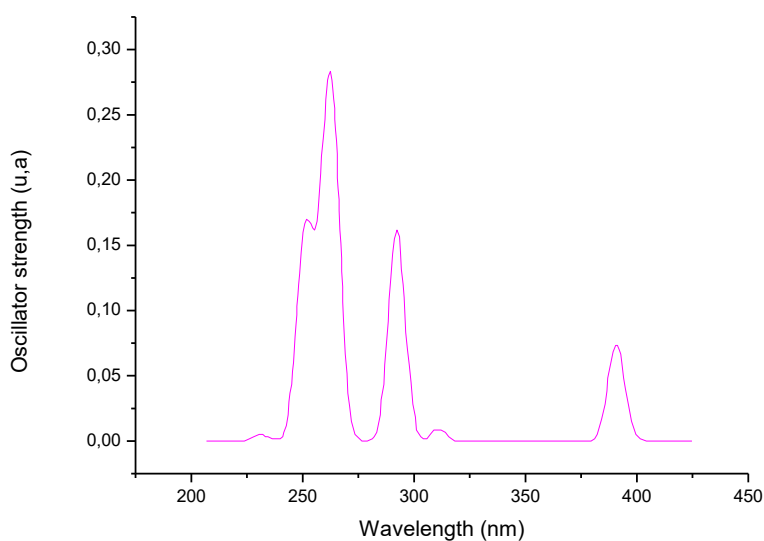
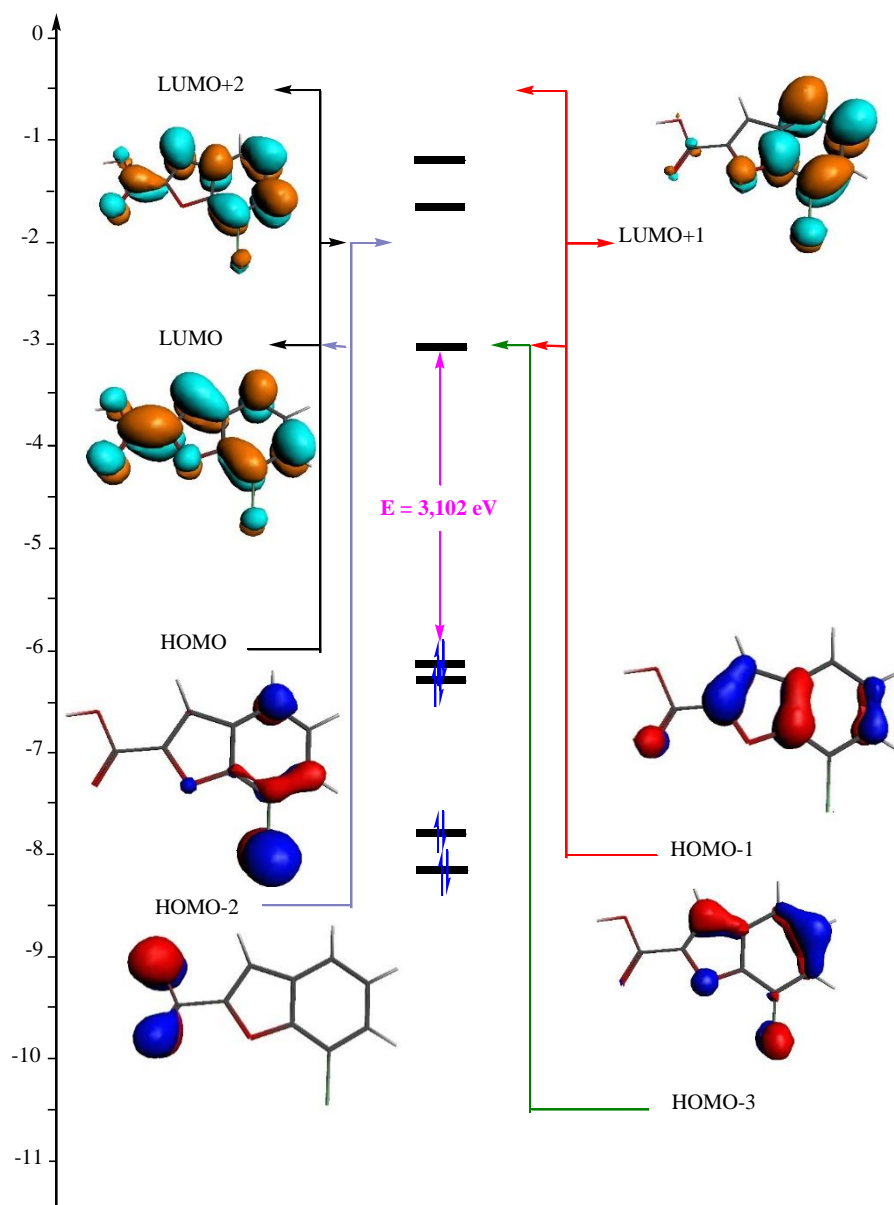


Figure 5. Theoretical electronic spectra for 4-Chlorobenzofuran-2-carboxylic acid (3a)

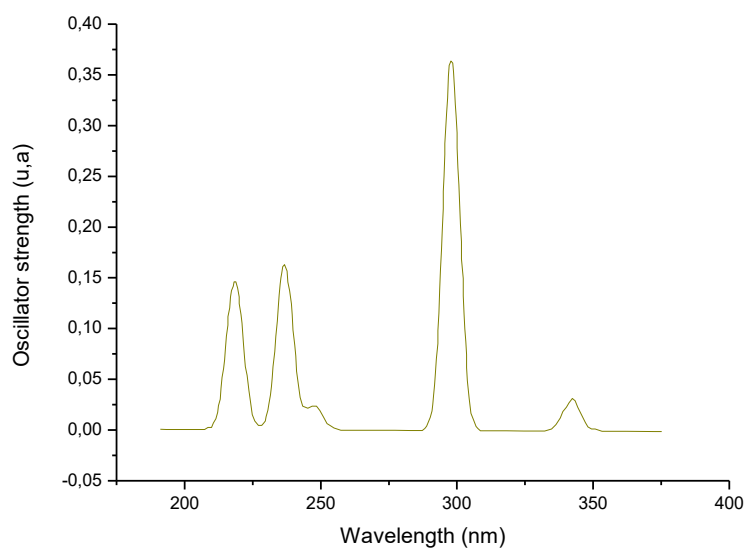


**Figure 6.** Diagram of electronic transitions of the 4-Chlorobenzofuran-2-carboxylic acid (3a)

#### II.4-Electronic spectra of 7-methylbenzofuran-2-carboxylic acid (4a)

In the compound 4a, the strong absorption band appears in the ultraviolet region centered at 298 nm. Happened essentially from the HOMO-1 ( $n$  C-O of furan +  $\pi$  (C-C of benzene and furan  $\rightarrow \pi^*$ )) (60,9%) and HOMO ( $n$  C=O carboxylic +  $\pi$  C-C of benzofuran  $\rightarrow \pi^*$ ) (27,9 %) to LUMO with an oscillator strength 0,369 (u.a).

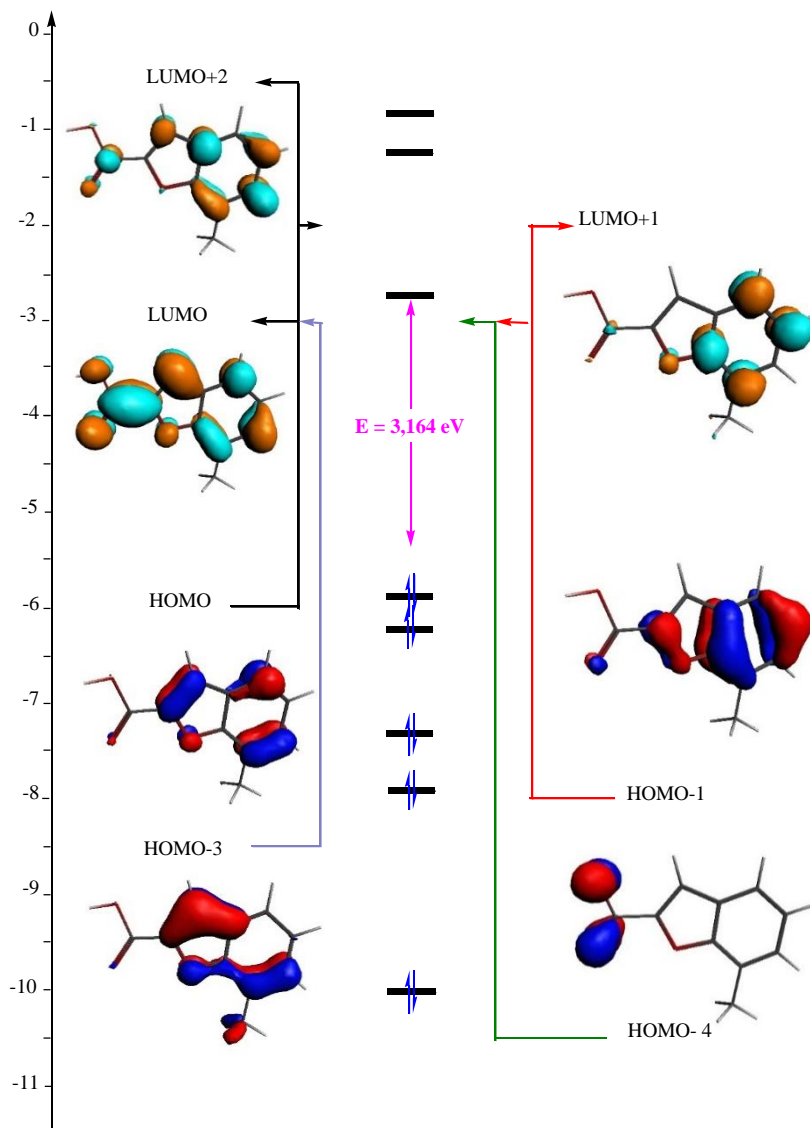
There is not a big difference between spectra of the compounds 4a and 1a, just in the first band; it was shifted by about 18 nm to the red



**Figure 7.** Theoretical electronic spectra for 7-Methylbenzofuran-2-carboxylic acid (4a)

**Table 4.** Calculated electronic transitions and their assignments of the compound 4a.

Excitation energies	$\lambda$ (nm)	Oscillator strengths	Electronique transition	Compositi on	Assignments
3,62	342	0,031	HOMO $\rightarrow$ LUMO HOMO-1 $\rightarrow$ LUMO	63,2% 30,3%	n+ $\pi$ $\rightarrow$ $\pi^*$ n+ $\pi$ $\rightarrow$ $\pi^*$
4,16	298	0,369	HOMO-1 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO	60,9% 27,9%	n+ $\pi$ $\rightarrow$ $\pi^*$ n+ $\pi$ $\rightarrow$ $\pi^*$
5,01	247	0,023	HOMO-3 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+1	42,5% 35,0%	n+ $\pi$ $\rightarrow$ $\pi^*$ n+ $\pi$ $\rightarrow$ $\pi^*$
5,24	237	0,164	HOMO $\rightarrow$ LUMO+2 HOMO $\rightarrow$ LUMO+1 HOMO-3 $\rightarrow$ LUMO HOMO-1 $\rightarrow$ LUMO+1	27,9% 20,7% 18,9% 18,7%	n+ $\pi$ $\rightarrow$ $\pi^*$ n+ $\pi$ $\rightarrow$ $\pi^*$ n+ $\pi$ $\rightarrow$ $\pi^*$ n+ $\pi$ $\rightarrow$ $\pi^*$
5,67	219	0,117	HOMO-1 $\rightarrow$ LUMO+1	27,9%	n+ $\pi$ $\rightarrow$ $\pi^*$
			HOMO $\rightarrow$ LUMO+1 HOMO-3 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+2	24,2% 17,2% 14,3%	n+ $\pi$ $\rightarrow$ $\pi^*$ n+ $\pi$ $\rightarrow$ $\pi^*$ n+ $\pi$ $\rightarrow$ $\pi^*$
5,71	217	0,032	HOMO-4 $\rightarrow$ LUMO	83,3%	n $\rightarrow$ $\pi^*$

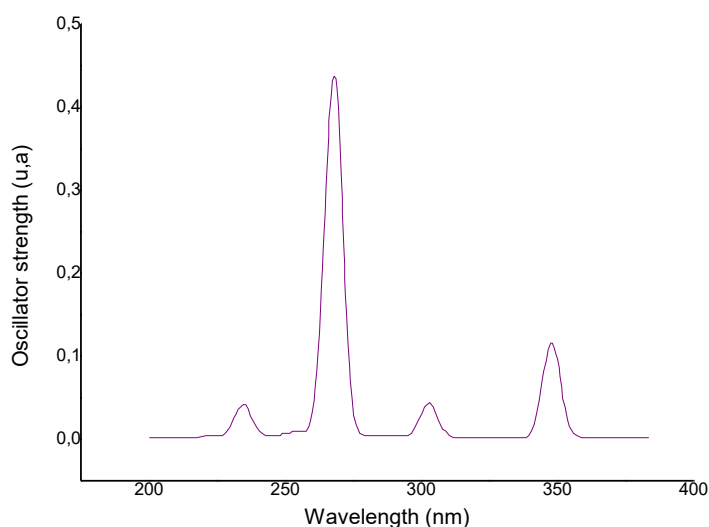


**Figure 8.** Diagram of electronic transitions of the 7-Methylbenzofuran-2-carboxylic acid (4a)

### II.5-Electronic spectra of 3-aminobenzofuran-2-carboxylic acid (5a)

In the compound 5a, the band found low energy centered at 348 nm due to the (n C=O carboxylic and furan+  $\pi$  C-C of furan  $\rightarrow \pi^*$ ) transitions corresponding to the HOMO $\rightarrow$ LUMO (86,0%) electronic transitions with an oscillator strength of 0,281 (u.a).

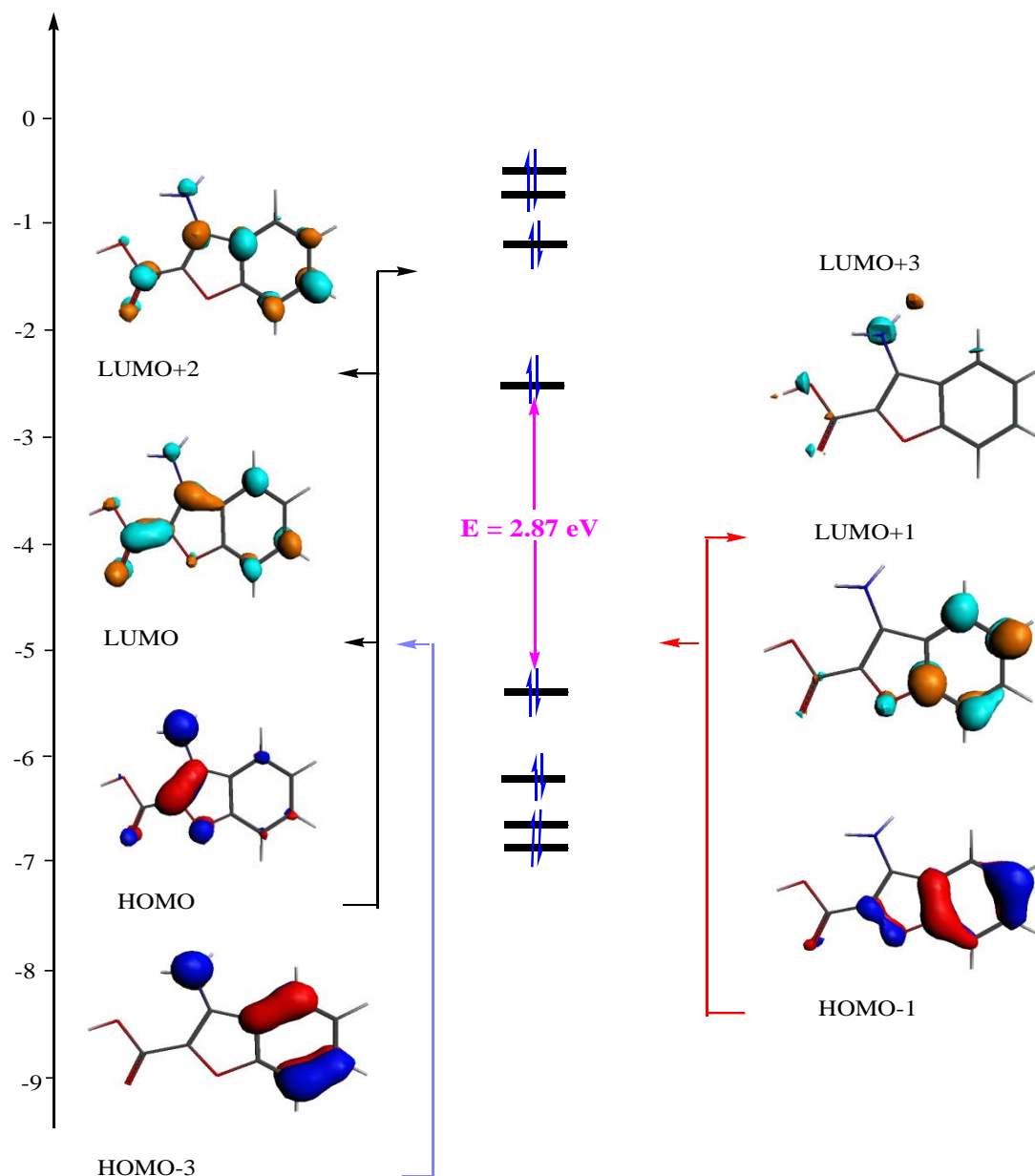
The tow electronic spectra of 5a and 4a, exhibit similar shapes but with somewhat differences concerning the bands positions and their widths.



**Figure 9.** Theoretical electronic spectra for 3-aminobenzofuran-2-carboxylic acid (5a)

**Table 5.** Calculated electronic transitions and their assignments of the compound 5a.

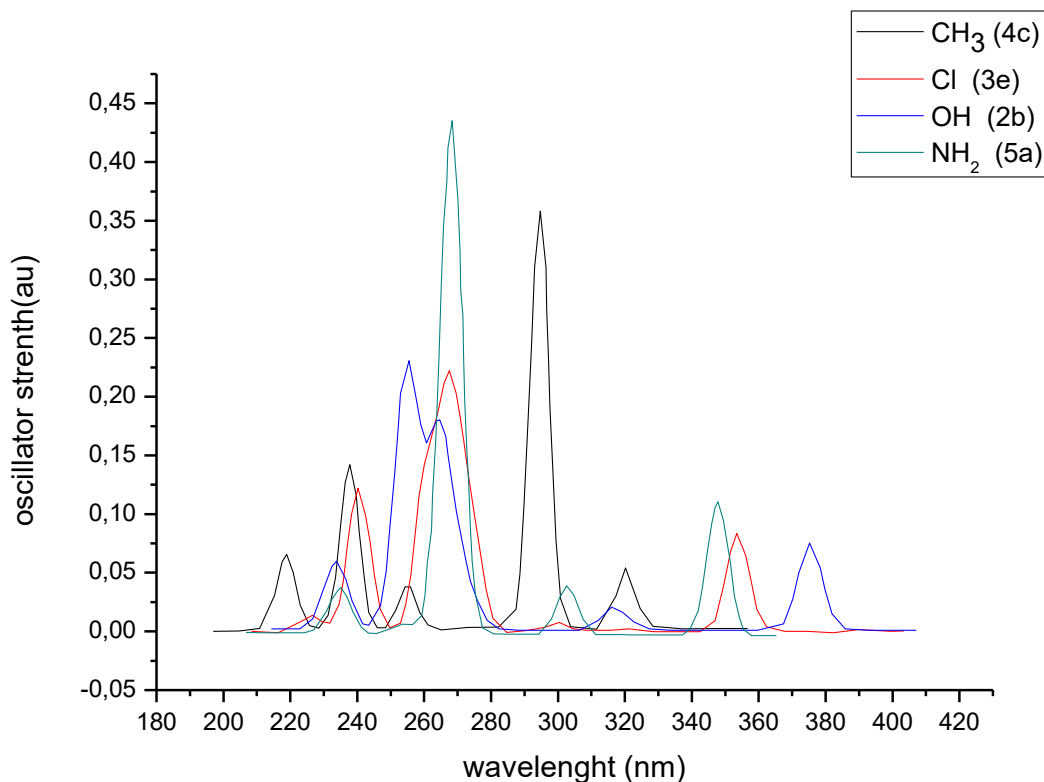
Excitation energies	$\lambda$ (nm)	Oscillator strengths	Electronic transition	Composition	Assignments
3,56	348	0,1140	HOMO $\rightarrow$ LUMO	86.0%	$n+\pi \rightarrow \pi^*$
4.09	303	0,0403	HOMO-1 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+1	52.9% 42.9%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
4,60	269	0,0501	HOMO-3 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO+2	67.1% 26.6%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
4.63	267	0,3918	HOMO $\rightarrow$ LUMO+1 HOMO-1 $\rightarrow$ LUMO HOMO $\rightarrow$ LUMO	48.1% 35.3% 7.1%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
5.28	234	0,0379	HOMO $\rightarrow$ LUMO+2 HOMO-3 $\rightarrow$ LUMO HOMO-1 $\rightarrow$ LUMO+1 HOMO $\rightarrow$ LUMO+3	49.7% 15.4% 12.7% 9.7%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$



**Figure 10.** Diagram of electronic transitions of the 3-aminobenzofuran-2-carboxylic acid (5a)

### II.6-Electronic spectra of benzofuran-2-carboxylic acid monosubstituted in furan ring

TD-DFT calculations were performed to determine the excitation energies and associated oscillator forces of the studied compounds (2b, 3e, 4c, 5a), in order to deduce their electronic spectra. Figure 11 shows the different absorption spectra simulated for the 2b, 3e, 4c, 5a compounds in gas phase.



**Figure 11.** Theoretical electronic spectra for benzofuran-2-carboxylic acid monosubstituted in furan ring (5a, 2b, 3e, 4c)

The spectra of each compound contain five absorption bands. The first less intense low energy bands (310-390 nm) attributed to the  $(n \text{ C=O and OH or Cl} + \pi \text{ C-C of benzene} \rightarrow \pi^* \text{ C-C})$  electronic transitions assigned to HOMO  $\rightarrow$  LUMO (85 %) transitions.

The shift towards the lower energies from 324 for 1a (see figure 1 and Table 1) to 348, 353 and 375 nm for 5a, 3e and 2b respectively (see Tables A5 and 5 and Figure 11), is proportional to the strength of electron-withdrawing groups.

The absorption spectrum of 4c compound shows a small blue shift in the lower energy absorption band compared to 1a (hypsochromic effect).

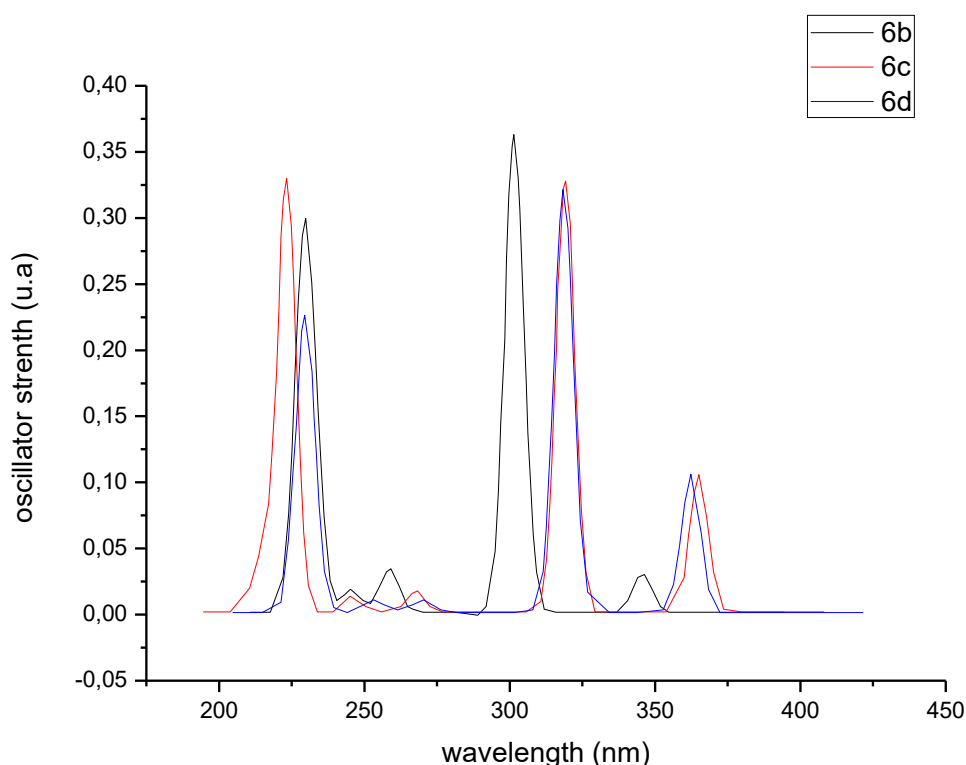
## II.7-Electronic spectra of di and tri substituted benzofuran-2-carboxylic acid

The theoretical electronic spectrum (Figure 12) of the compound 5-chloro-3-methylbenzofuran-2-carboxylic acid (6b) shows six absorption bands. The first broadest band centered at 346 nm correspond to the  $(n \text{ (C-O, O furan and Cl)} + \pi \text{ C-C of benzofuran} \rightarrow \pi^*)$  and  $(n \text{ C-O of furan} + \pi \text{ C-C benzofuran} \rightarrow \pi^*)$  electronic transitions assigned to

HOMO-1→LUMO (55,5%) and HOMO→LUMO (38,4%) transitions with an oscillator strength 0,0293 (u.a).

The second important band in the region of 290-310 nm corresponding to the HOMO→LUMO (54,6%) and HOMO-1→LUMO (35,1%) electronic transitions with an oscillator strength of 0,3626 (u.a).

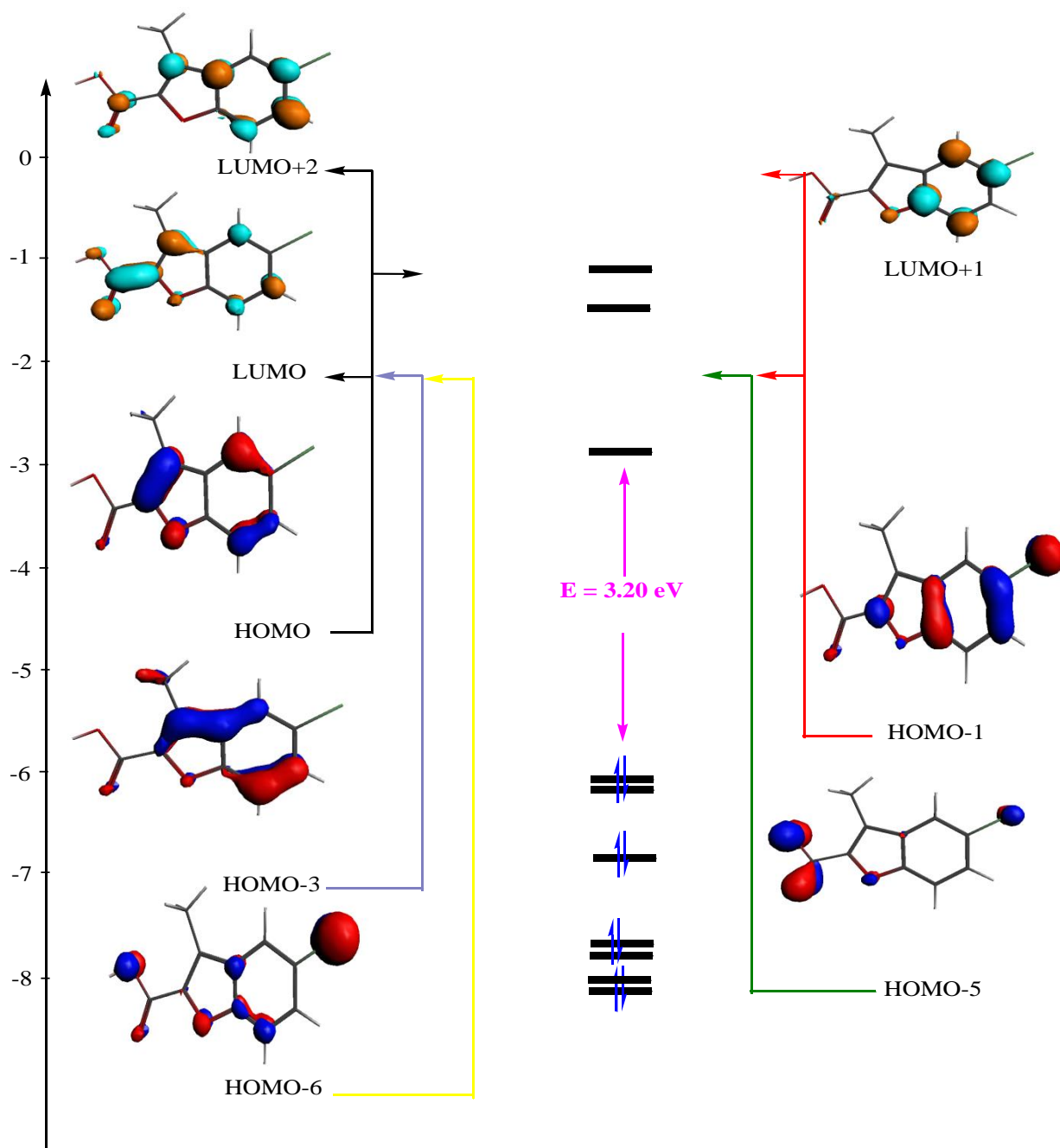
The third band centered at 259 nm assigned to HOMO→LUMO+1, HOMO-3→LUMO (n C-O of furan +  $\pi$  C-C of benzofuran→ $\pi^*$ ) and HOMO-1→LUMO+1 transitions with an oscillator strength 0,0334.



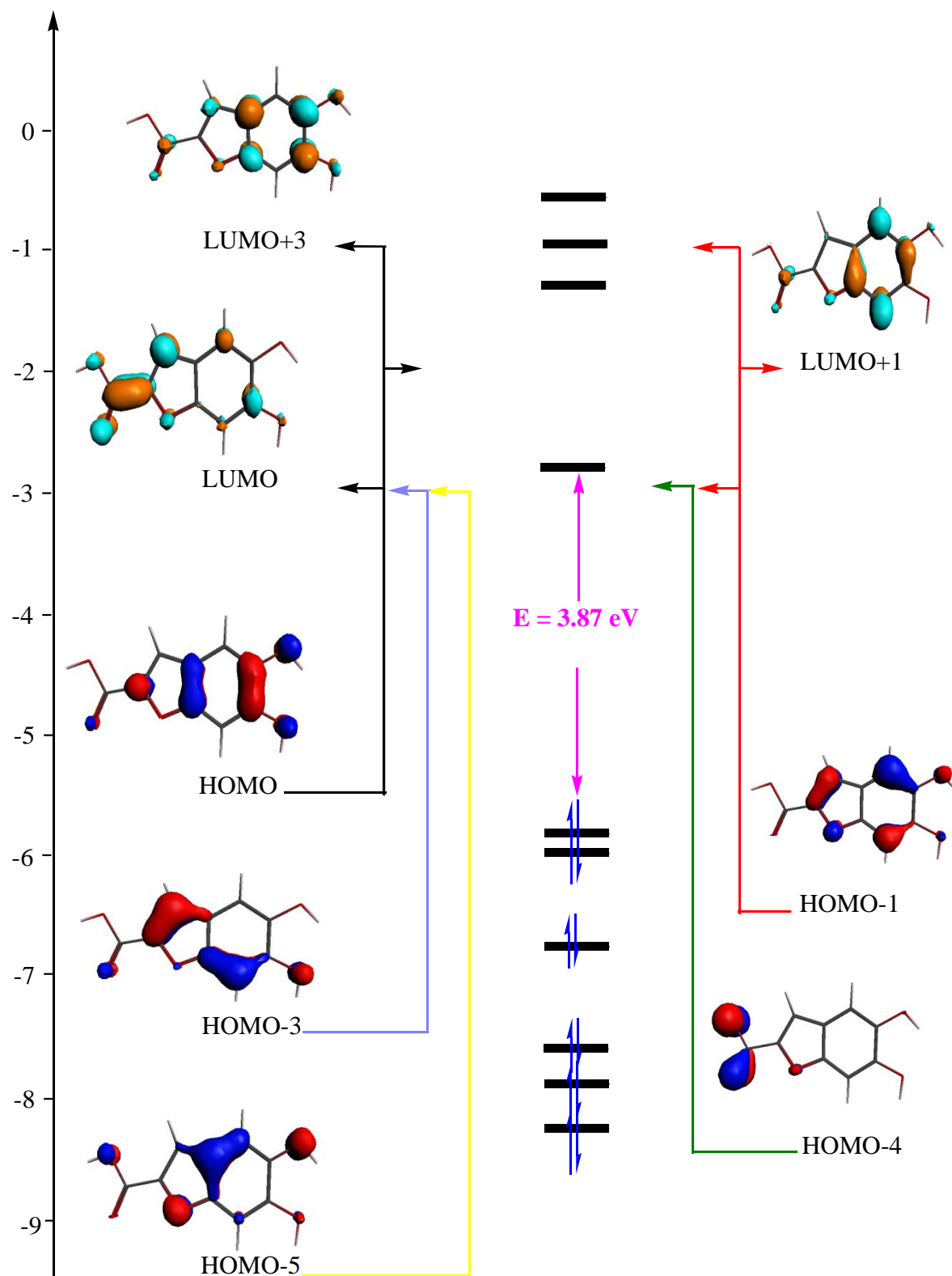
**Figure 12.** Theoretical electronic spectra 6b, 6c, 6c compounds

The theoretical electronic spectrum (Figure 12) of 5,6-dihydroxybenzofuran-2-carboxylic acid (6c), shows absorption band appears in the ultraviolet region centered at 366 nm corresponding to the (n C-O and n O furan) + $\pi$  C-C of benzofuran → $\pi^*$ ) transitions. These transitions corresponding to excitations from HOMO→LUMO (64,2%) and HOMO-1→LUMO (30,4%).

The band found low energy centered at 320 nm, corresponding to ( $n$  C-O and O furan +  $\pi$  C-C of benzene and furan  $\rightarrow \pi^*$ ) assigned to HOMO-1  $\rightarrow$  LUMO and HOMO  $\rightarrow$  LUMO electronic transitions, which is shifted by about 20 nm than that to the compound 6b.



**Figure 13.** Diagram of electronic transitions of the 5-Chloro-3-Methylbenzofuran-2-carboxylic acid (6b)



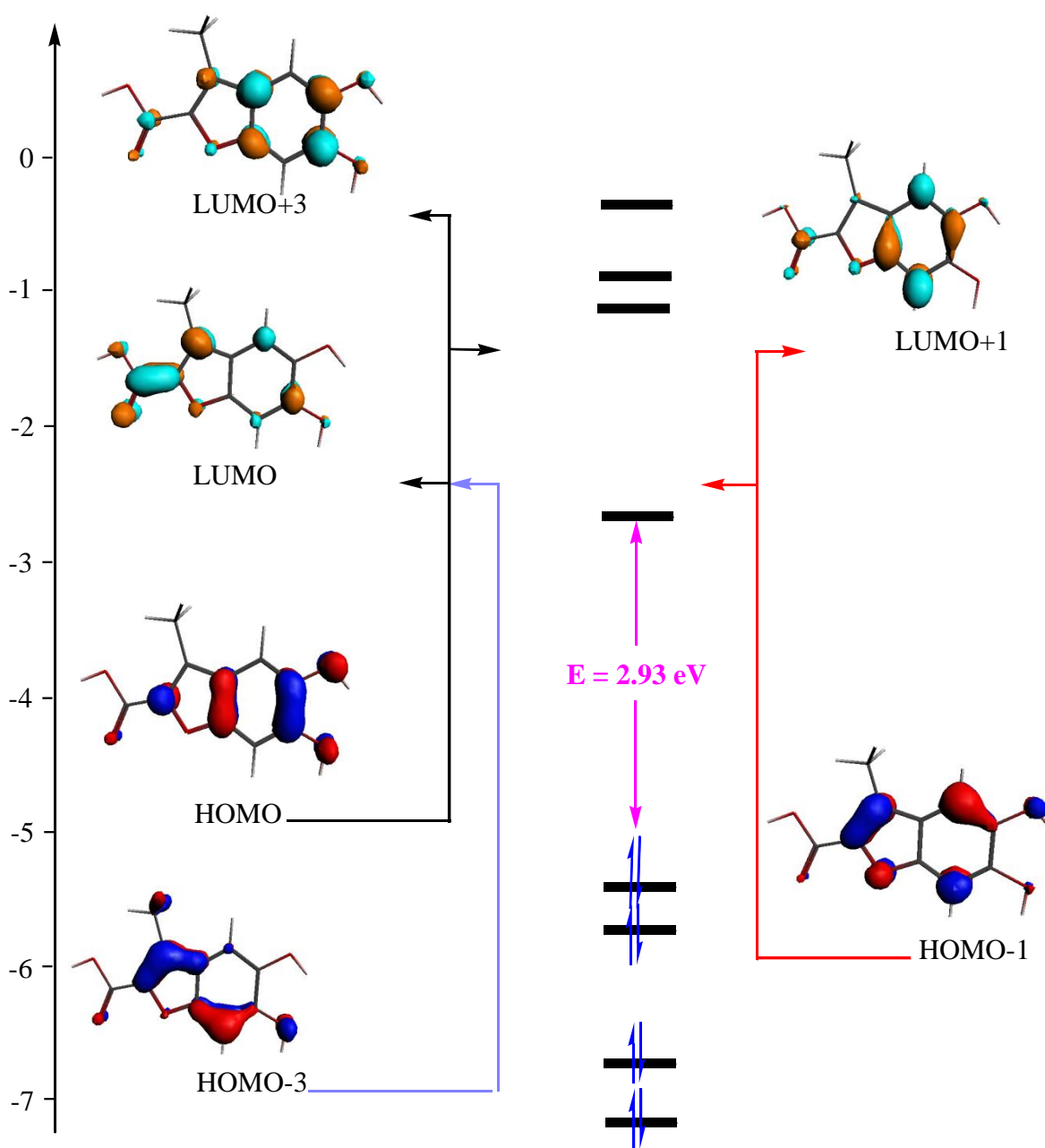
**Figure 14.** Diagram of electronic transitions of the 5,6-dihydroxybenzofuran-2-carboxylic acid (6c)

**Table 6.** Calculated electronic transitions and their assignments of 6b, 6c, 6d compounds

excitation energies	$\lambda$ (nm)	oscillator strengths	Electronic transition	composition	assignments
<b>5-Chloro-3-Methylbenzofuran-2-carboxylic acid (6b)</b>					
3,58	346	0,0293	HOMO-1→LUMO HOMO→LUMO	55,5% 38,4%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
4,10	302	0,3626	HOMO→LUMO HOMO-1→LUMO	54,6% 35,1%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
4,79	259	0,0334	HOMO→LUMO+1 HOMO-3→LUMO	41,5% 37,9%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
5,05	246	0,0177	HOMO-1→LUMO+1 HOMO→LUMO+2 HOMO-3→LUMO	39,0% 34,9% 12,2%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
5,35	232	0,1720	HOMO→LUMO+1 HOMO-3→LUMO HOMO-1→LUMO+1	40,3% 19,8% 14,7%	$n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
5,42	229	0,1588	HOMO-6→LUMO HOMO-5→LUMO HOMO-1→LUMO+2	44,2% 41,5% 6,1%	$n \rightarrow \pi^*$ $n \rightarrow \pi^*$ $n+\pi \rightarrow \pi^*$
<b>5,6-dihydroxybenzofuran-2-carboxylic acid (6c)</b>					
3,39	366	0,1048	HOMO→LUMO HOMO-1→LUMO	64,2% 30,4%	$\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$
3,88	320	0,3305	HOMO-1→LUMO HOMO→LUMO	61,8% 28,8%	$\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$
4,63	268	0,0176	HOMO→LUMO+1 HOMO-3→LUMO	73,9% 9,8%	$\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$
5,04	246	0,132	HOMO-1→LUMO+1 HOMO-3→LUMO HOMO-1→LUMO+3	47,3% 20,8% 9,8%	$\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$
5,54	224	0,3247	HOMO-3→LUMO HOMO-1→LUMO+1	45,5% 28,2%	$\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$
5,64	220	0,0134	HOMO-4→LUMO	86,9%	$n \rightarrow \pi^*$
5,78	215	0,0372	HOMO-5→LUMO HOMO→LUMO+3	52,6% 31,8%	$\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$
<b>5,6-dihydroxy-3-methylbenzofuran-2-carboxylic acid (6d)</b>					
3,42	363	0,1058	HOMO→LUMO HOMO-1→LUMO	63,0% 31,3%	$\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$
3,89	319	0,3225	HOMO-1→LUMO HOMO→LUMO	61,1% 29,7%	$\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$
4,89	254	0,0102	HOMO→LUMO+1 HOMO-1→LUMO+1 HOMO-3→LUMO HOMO-1→LUMO+3	28,5% 27,4% 21,4% 13,9%	$\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$
5,40	230	0,2275	HOMO-1→LUMO+1 HOMO-3→LUMO	44,8% 36,0%	$\pi+n \rightarrow \pi^*$ $\pi+n \rightarrow \pi^*$

For the 5,6-dihydroxy-3-methylbenzofuran-2-carboxylic acid (6d) spectrum (Figure 12), the low energy absorption band appears essentially in the ultraviolet region centered at 363 nm corresponding to the (n (O-H and C-C of furan and  $\pi$  C-C of benzofuran  $\rightarrow \pi^*$ ) and (n (O-H and C-C of benzene and C-O furan) +  $\pi$  C-C of benzene and furan  $\rightarrow \pi^*$ ) transitions. These transitions corresponding to excitations from HOMO  $\rightarrow$  LUMO (63,0%). And HOMO-1  $\rightarrow$  LUMO (31,3%) electronic transitions

The two electronic spectra of 6d and 6c, exhibit similar shapes but with somewhat differences concerning the bands positions and their widths. This is due to the fact that the CH<sub>3</sub> group almost has no effect on the molecule spectra.



**Figure 15.** Diagram of electronic transitions of the 5,6-dihydroxy-3-methylbenzofuran-2-carboxylic acid (6d)

### III-Conclusion

In this chapter, we have carried out a theoretical analysis of spectroscopic aspects of Benzofuran-2-carboxylic acid and its derivatives. We understand the effect of the inserted groups on the optical properties of the Benzofuran-2-carboxylic acid.

The theoretical results obtained in the case of hydroxy, amino and chlorobenzofuran-2-carboxylic acid show that the addition of electron-withdrawing groups causes a red shift of the absorption band (bathochromic effect). For the CH<sub>3</sub> substituted in furan ring, the results show small blue shift of the low-energy absorption band

The addition of more substituents causes a blue shift of the absorption band (hypsochromic effect) compared to mono substituted compounds

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**GENERAL CONCLUSION**

### General conclusion

During our thesis work, we are interested in the theoretical study of Benzofuran-2-carboxylic acid and derivatives which have applications in the pharmaceutical field. This work was carried out using a quantum method based on density functional theory (DFT).

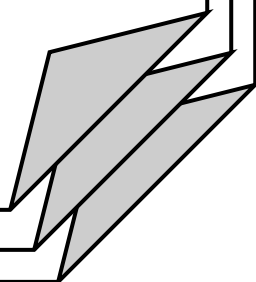
In order to determine the substituent effects of benzofuran-2-carboxylic acid substituted at different position of the phenyl and furan rings by OH, Cl, NH<sub>2</sub> and CH<sub>3</sub> groups, the analysis of structural and electronic properties of the Benzofuran-2-carboxylic acid and derivatives show that the addition of electron-withdrawing groups has only a minor effect on the structural parameters (bond lengths and angles).

The OH, Cl and NH<sub>2</sub> groups destabilize the energies of the HOMO and LUMO of Benzofuran-2-carboxylic acid and as result the HOMO-LUMO gaps decreased. Consequently HOMO-LUMO energy gap play an important role in the determination of the UV-visible spectra.

A theoretical analysis of spectroscopic properties of Benzofuran-2-carboxylic acid and its substituted compounds were performed. They are largely affected by the introducing of the electron-withdrawing substituents (Cl, OH and NH<sub>2</sub>) on the phenyl or furan rings. There is a shift of 60 nm towards the lower energies in the absorption bands (bathochromic effect). For the CH<sub>3</sub> substituted in furan ring, the results show a small blue shift of the low-energy absorption band.

On the other hand, the addition of more substituents causes a blue shift of the absorption band (hypsochromic effect) compared to mono substituted compounds.

# **Annexes**



**Annex I**

**Tables**

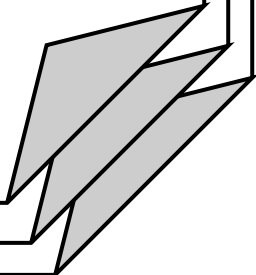


Table A1. Hirshfeld charges and  $\mu$  dipole moments (Debye) of hydroxybenzofuran-2-carboxylic acid isomers (2a, 2b, 2c, 2d and 2e)

	2a	2b	2c	2d	2e
C1	-0,077	-0,053	-0,087	0,049	-0,056
C5	-0,041	-0,043	0,058	-0,073	-0,083
C6	-0,062	-0,050	-0,086	-0,048	0,053
C7	0,078	0,071	0,071	0,055	0,040
C8	-0,031	-0,037	-0,036	-0,022	-0,023
C9	0,078	-0,043	-0,044	-0,091	-0,070
C4	-0,051	0,037	-0,074	-0,078	-0,071
C3	0,044	-0,019	0,025	0,033	0,031
C10	0,169	0,109	0,117	0,121	0,122
O2	-0,061	-0,035	-0,076	-0,074	-0,087
O12	-0,256	-0,195	-0,198	-0,194	-0,197
O13	-0,168	-0,092	-0,099	-0,096	-0,092
O19	-0,166	-0,078	-0,081	-0,089	-0,076
H11	0,056	0,055	0,052	0,055	0,170
H17	0,047	0,044	0,166	0,042	0,040
H18	0,041	0,042	0,034	0,164	0,041
H15	0,169	0,046	0,046	0,035	0,040
H16	0,062	0,127	0,050	0,048	0,052
H14	0,170	0,164	0,161	0,163	0,164
$\mu$	3,910	2,481	3,667	3,519	1,208

**Table A2.** Hirshfeld charges and  $\mu$  dipole moments (Debye) of Chlorobenzofuran-2-carboxylic acid isomers (3a, 3b, 3c, 3d and 3e)

	3a	3b	3c	3d	3e
C1	-0,058	-0,071	-0,008	-0,052	-0,049
C5	-0,036	-0,001	-0,062	-0,068	-0,041
C6	-0,047	-0,070	-0,045	-0,010	-0,047
C7	0,080	0,073	0,066	0,053	0,071
C8	-0,027	-0,025	-0,019	-0,020	-0,036
C9	0,021	-0,040	-0,065	-0,053	-0,045
C4	-0,052	-0,071	-0,071	-0,070	-0,033
C3	0,051	0,034	0,038	0,038	0,011
C10	0,172	0,125	0,127	0,127	0,116
O2	-0,057	-0,071	-0,070	-0,071	-0,072
O12	-0,251	-0,201	-0,199	-0,199	-0,206
O13	-0,164	-0,092	-0,090	-0,090	-0,099
Cl	0,026	0,049	0,035	0,065	0,076
H11	0,060	0,053	0,059	0,041	0,057
H17	0,052	0,040	0,042	0,045	0,046
H15	0,049	0,050	0,044	0,046	0,044
H16	0,060	0,053	0,053	0,054	0,041
H14	0,173	0,165	0,166	0,165	0,164
$\mu$	1,493	2,523	1,773	2,577	1,939

**Table A3.** Hirshfeld charges and  $\mu$  dipole moments (Debye) of methylbenzofuran-2-carboxylic acid (4a, 4b, 4c, 4d and 4e)

	4a	4b	4c	4d	4e
C1	-0,053	-0,054	-0,052	-0,052	0,007
C5	-0,043	-0,042	-0,041	0,017	-0,040
C6	0,008	-0,052	-0,047	-0,050	-0,048
C7	0,076	0,076	0,076	0,076	0,074
C8	-0,019	-0,019	-0,019	-0,020	-0,019
C9	-0,046	0,017	-0,040	-0,041	-0,044
C4	-0,054	-0,053	0,005	-0,054	-0,054
C3	0,045	0,045	0,041	0,044	0,045
C10	0,169	0,169	0,168	0,167	0,169
O2	-0,057	-0,062	-0,066	-0,062	-0,062
O12	-0,256	-0,255	-0,259	-0,256	-0,255
O13	-0,169	-0,170	-0,159	-0,170	-0,169
C19	-0,104	-0,106	-0,106	-0,106	-0,108
H11	0,104	0,056	0,057	0,054	0,057
H17	0,042	0,046	0,046	0,106	0,045
H18	0,043	0,041	0,043	0,043	0,108
H15	0,046	0,046	0,045	0,047	0,044
H16	0,059	0,058	0,048	0,059	0,059
H14	0,170	0,170	0,169	0,170	0,170
$\mu$	2,263	3,262	3,069	3,137	3,260

**Table A4.** Hirshfeld charges and  $\mu$  dipole moments (Debye) of aminobenzofuran-2-carboxylic acid (5a, 5b, 5c, 5d and 5e)

	5a	5b	5c	5d	5e
C1	-0,052	-0,074	-0,065	-0,055	0,043
C5	-0,040	-0,043	0,054	-0,064	-0,053
C6	-0,046	-0,068	-0,070	0,045	-0,048
C7	0,077	0,076	0,076	0,063	0,066
C8	-0,026	-0,031	-0,029	-0,019	-0,020
C9	-0,042	0,054	-0,041	-0,062	-0,065
C4	0,043	-0,057	-0,056	-0,053	-0,059
C3	0,016	0,042	0,038	0,044	0,044
C10	0,157	0,167	0,164	0,168	0,168
O2	-0,074	-0,061	-0,066	-0,063	-0,064
O12	-0,266	-0,257	-0,262	-0,259	-0,257
O13	-0,168	-0,172	-0,174	-0,169	-0,170
N	-1,169	-0,177	-0,178	-0,176	-0,190
H11	0,058	0,053	0,053	0,176	0,057
H17	0,047	0,045	0,178	0,042	0,044
H18	0,044	0,039	0,041	0,042	0,190
H15	0,044	0,177	0,048	0,043	0,044
H16	0,125	0,056	0,058	0,060	0,058
H14	0,167	0,169	0,167	0,170	0,169
$\mu$	4,033	4,368	4,211	2,071	4,125

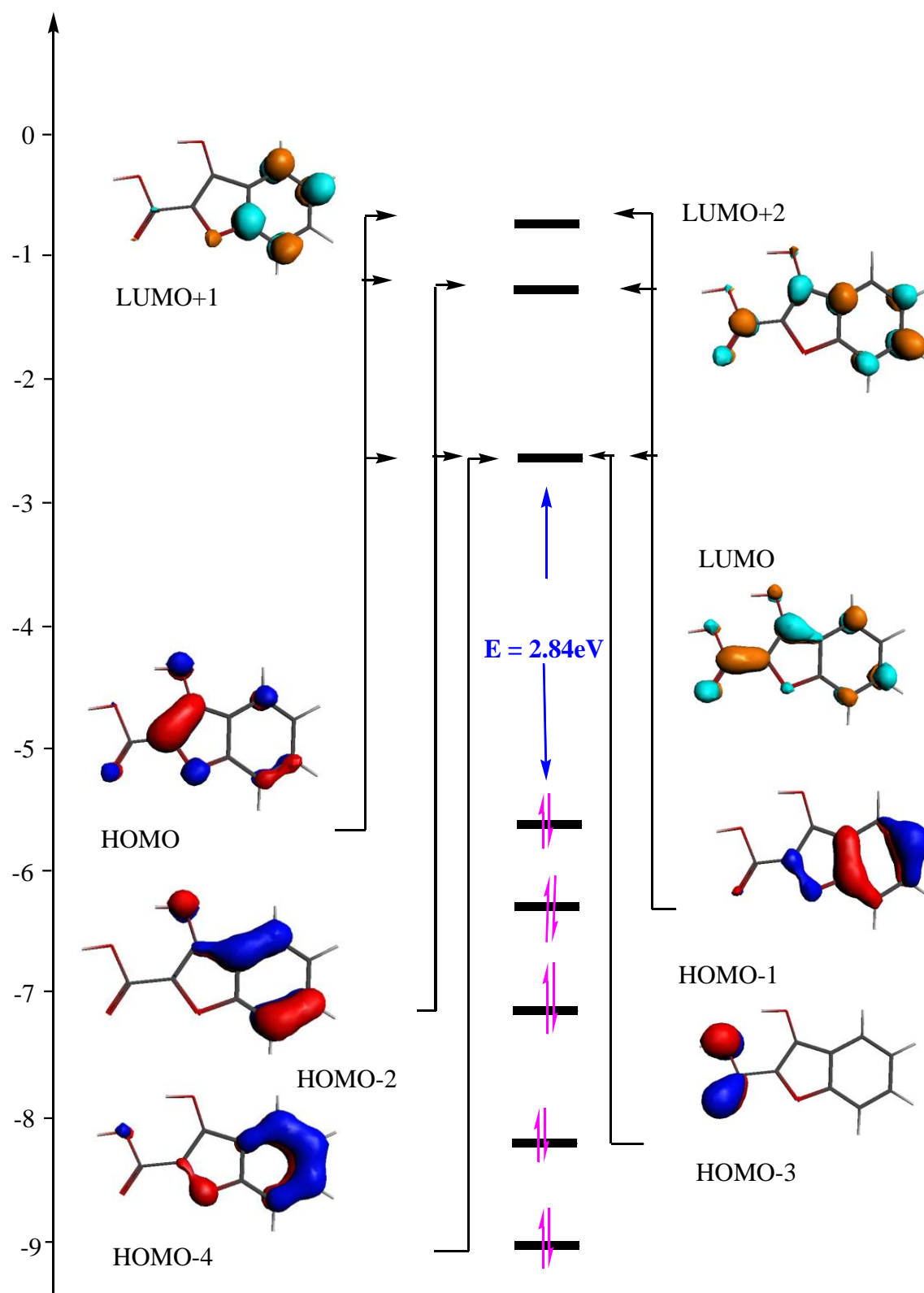
**Table A5.** Calculated electronic transitions and their assignments, the dominant contributions to electron excitations in percentages (%), wavelengths  $\lambda$  (nm), oscillator strengths  $f$  (au), and excitation energies (eV) of compounds 2b, 3e, 4c, 6a obtained in gas phase

excitation energies	$\lambda$ (nm)	oscillator strengths	Electronic transition	composition	Assignments
3-hydroxybenzofuran-2-carboxylic acid (2b)					
3,30	375	0,1098	HOMO→LUMO	78.8%	$n+\pi \rightarrow \pi^*$
			HOMO-1→LUMO	14.9%	$n+\pi \rightarrow \pi^*$
4.17	297	0,1486	HOMO-1→LUMO	58.6%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+1	28.8%	$n+\pi \rightarrow \pi^*$
4,69	264	0,1829	HOMO-2→LUMO	52.1%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+1	16.5%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+2	16.0%	$n+\pi \rightarrow \pi^*$
4.90	253	0,1921	HOMO→LUMO+1	46.4%	$n+\pi \rightarrow \pi^*$
			HOMO-2→LUMO	16.5%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+2	13.1 %	$n+\pi \rightarrow \pi^*$
5.82	213	0,0127	HOMO-1→LUMO+2	30.6%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+2	19.7%	$n+\pi \rightarrow \pi^*$
			HOMO-3→LUMO	14.4%	$n+\pi \rightarrow \pi^*$
6.03	205	0.0297	HOMO-3→LUMO	67.6%	$n+\pi \rightarrow \pi^*$
6.27	197	0.2796	HOMO-1→LUMO+1	39.3%	$n+\pi \rightarrow \pi^*$
			HOMO-4→LUMO	17.1%	$n+\pi \rightarrow \pi^*$
			HOMO-1→LUMO+1	13.0%	$n+\pi \rightarrow \pi^*$
3-Chlorobenzofuran-2-carboxylic acid (3e)					
3,55	349	0,0847	HOMO→LUMO	84.8%	$n+\pi \rightarrow \pi^*$
4,17	297	0,0104	HOMO→LUMO+1	63.1%	$n+\pi \rightarrow \pi^*$
			HOMO-2→LUMO	31.6%	$n+\pi \rightarrow \pi^*$
4,56	271	0,0459	HOMO-3→LUMO	43.6%	$n+\pi \rightarrow \pi^*$
			HOMO-2→LUMO	19.1%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+1	14.9%	$n+\pi \rightarrow \pi^*$
4,64	267	0,3000	HOMO-2→LUMO	32.4%	$n+\pi \rightarrow \pi^*$
			HOMO-3→LUMO	32,2%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+1	9.7%	$n+\pi \rightarrow \pi^*$
4.87	254	0,0548	HOMO-1→LUMO+1	82.8%	$n+\pi \rightarrow \pi^*$
5,17	239	0,1157	HOMO→LUMO+2	75.5%	$n+\pi \rightarrow \pi^*$
			HOMO-3→LUMO	11.8%	$n+\pi \rightarrow \pi^*$
5.54	223	0.0138	HOMO-1→LUMO+2	53.2%	$n+\pi \rightarrow \pi^*$
			HOMO-2→LUMO+1	18.1%	$n+\pi \rightarrow \pi^*$
			HOMO-3→LUMO+1	10.9%	$n+\pi \rightarrow \pi^*$

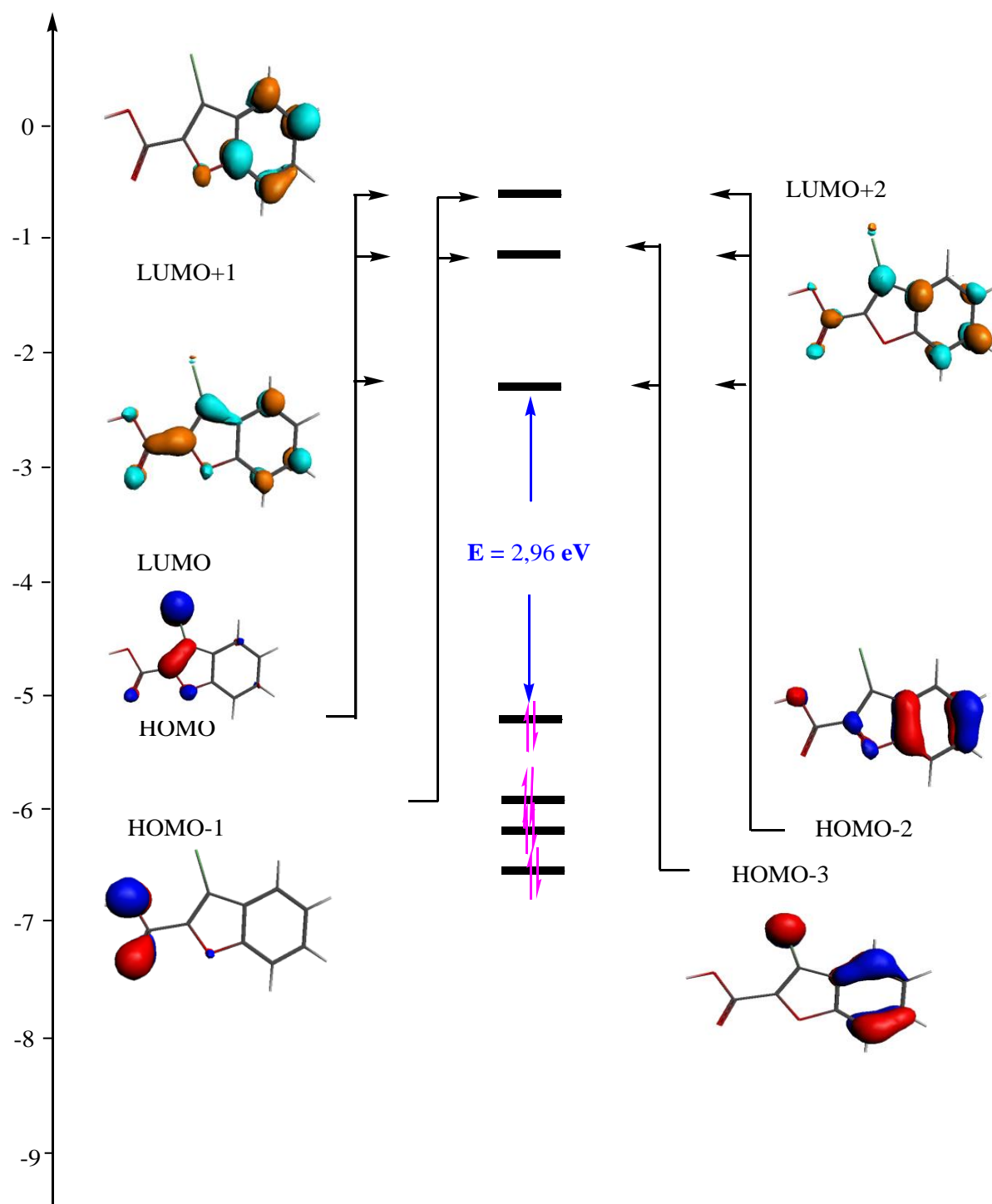
**Table 5A** (continued).

excitation energies	$\lambda$ (nm)	oscillator strengths	Electronic transition	composition	Assignments
3-Methylbenzofuran-2-carboxylic acid (4c)					
3,82	324	0,0480	HOMO→LUMO	48.0%	$n+\pi \rightarrow \pi^*$
			HOMO-1→LUMO	45.0%	$n+\pi \rightarrow \pi^*$
			HOMO-1→LUMO	44.1%	$n+\pi \rightarrow \pi^*$
4,19	295	0,3612	HOMO→LUMO	43.9%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+1	6.3%	$n+\pi \rightarrow \pi^*$
4,82	257	0,0276	HOMO-3→LUMO	46.3%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+1	38.4%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+2	10.6%	$n+\pi \rightarrow \pi^*$
5.19	238	0,1385	HOMO→LUMO+1	34.7%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+2	21.9%	$n+\pi \rightarrow \pi^*$
			HOMO-3→LUMO	17.2%	$n+\pi \rightarrow \pi^*$
5.62	220	0,0432	HOMO-4→LUMO	51.1%	$n+\pi \rightarrow \pi^*$
			HOMO-1→LUMO+1	18.0%	$n+\pi \rightarrow \pi^*$
			HOMO-1→LUMO+2	6.4%	$n+\pi \rightarrow \pi^*$
5,65	219	0,0116	HOMO-4→LUMO	34.6%	$n+\pi \rightarrow \pi^*$
			HOMO-1→LUMO+1	19.7%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+2	13.6%	$n+\pi \rightarrow \pi^*$
5,7-dimethylbenzofuran-2-carboxylic acid (6a)					
3,48	356	0,0260	HOMO→LUMO	79,0%	$n+\pi \rightarrow \pi^*$
			HOMO-1→LUMO	14,7	$n+\pi \rightarrow \pi^*$
4,10	302	0,3273	HOMO-1→LUMO	72,6%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO	11,8%	$n+\pi \rightarrow \pi^*$
			HOMO-3→LUMO	6,6%	$n+\pi \rightarrow \pi^*$
4,80	258	0,0769	HOMO-3→LUMO	68,8%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+1	8,3%	$n+\pi \rightarrow \pi^*$
5,07	245	0,1738	HOMO→LUMO+2	34,6%	$n+\pi \rightarrow \pi^*$
			HOMO-1→LUMO+1	32,2%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+1	16,2%	$n+\pi \rightarrow \pi^*$
5,32	233	0,0909	HOMO→LUMO+1	41,2%	$n+\pi \rightarrow \pi^*$
			HOMO→LUMO+2	22,2%	$n+\pi \rightarrow \pi^*$
			HOMO-6→LUMO	19,7 %	$n+\pi \rightarrow \pi^*$
5,58	222	0,0204	HOMO-5→LUMO	84,0%	$n+\pi \rightarrow \pi^*$

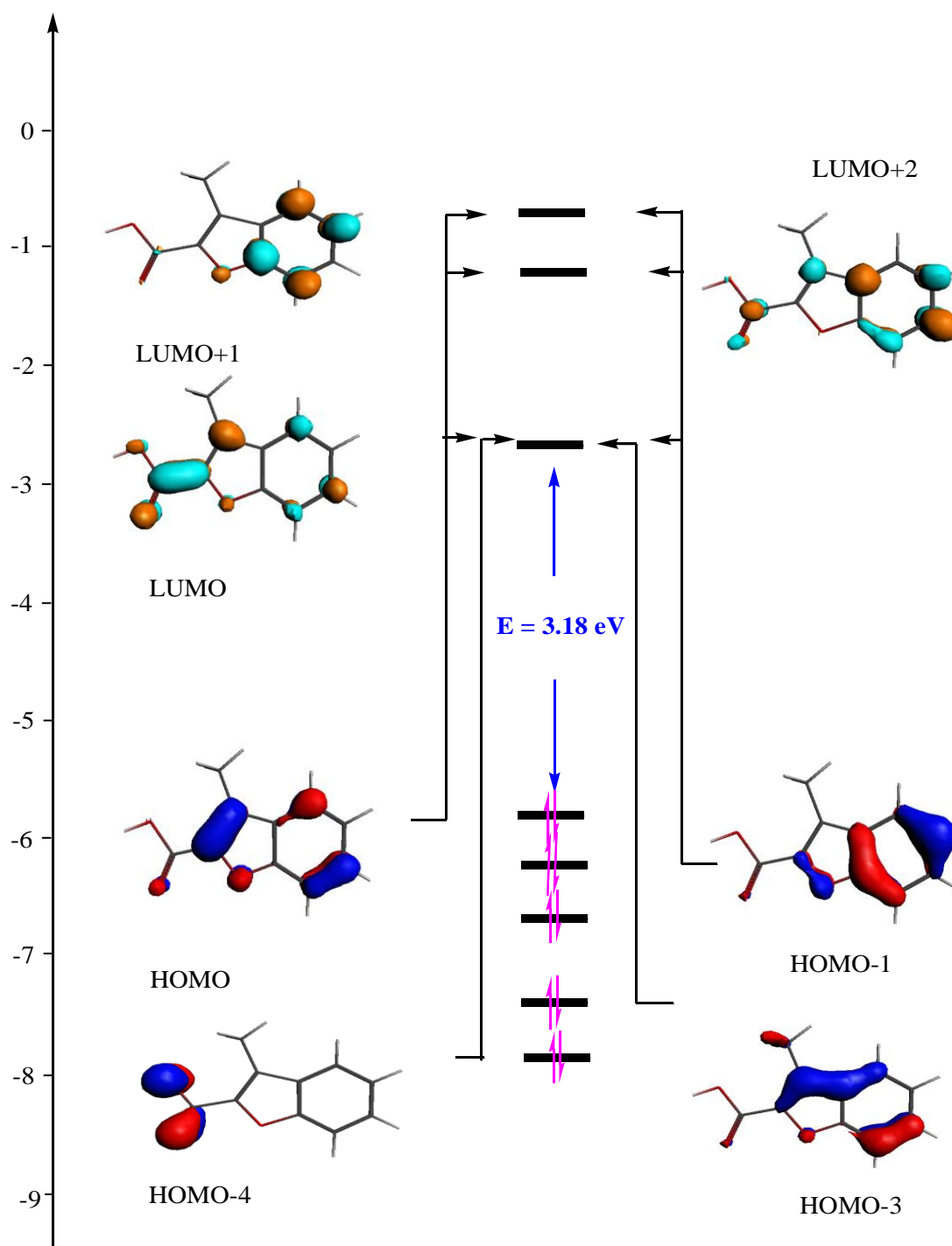
**Annex II**  
**Figures**



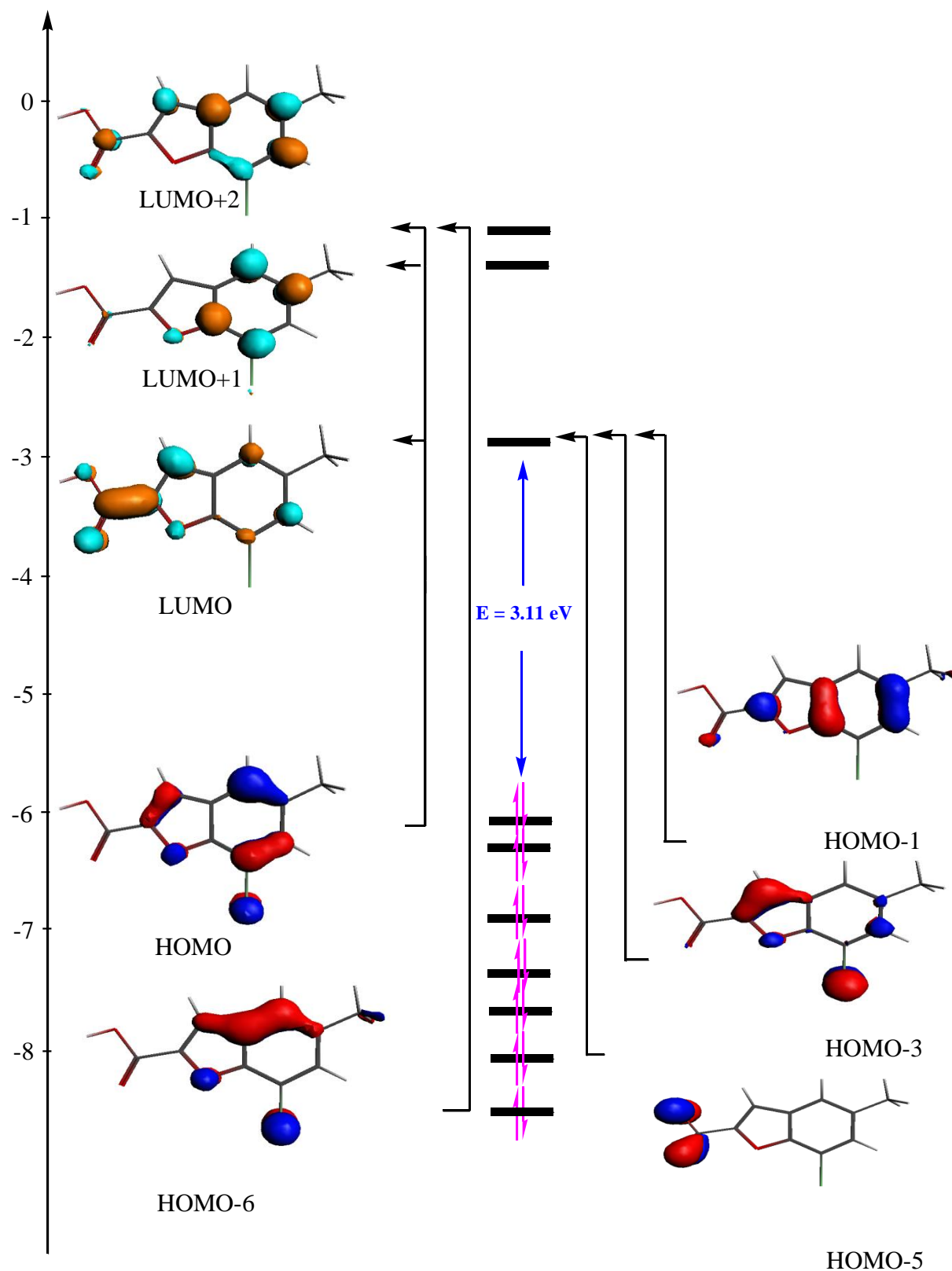
**Figure 1A.** Diagram of electronic transitions of the 3-hydroxybenzofuran-2-carboxylic acid (2b)



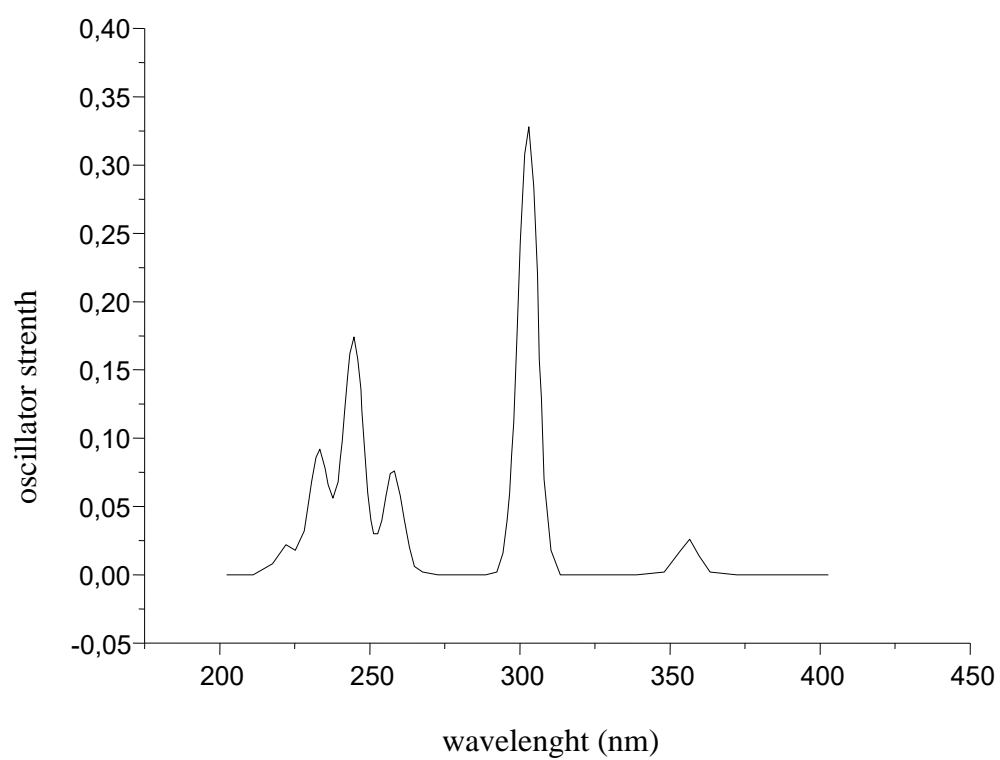
**Figure 2 A.** Diagram of electronic transitions of the 3-Chlorobenzofuran-2-carboxylic acid (3e)



**Figure 3A.** Diagram of electronic transitions of the 3-Methylbenzofuran-2-carboxylic acid (4c)

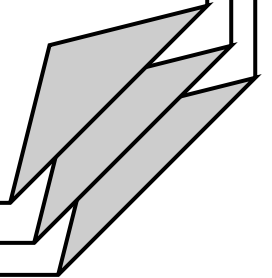


**Figure 4A.** Diagram of electronic transitions of the 5,7-dimethylbenzofuran-2-carboxylic acid (6a)



**Figure 5A.** Theoretical electronic spectra for 5,7-dimethylbenzofuran-2-carboxylic acid (6a)

**Abstract**



**Abstract**

A theoretical study based on density functional theory (DFT) was performed on Benzofuran-2-carboxylic acid and its derivatives including OH, Cl, NH<sub>2</sub> and CH<sub>3</sub> substituents. Structural optimization, electronic properties have been investigated using BP86/TZP level. The results reveal that electron-withdrawing groups has only a minor effect on the geometrical parameters and decreased the HOMO-LUMO energy gaps. By means of the TD-DFT method, the absorption spectra were calculated based on the optimized ground-state geometries. It is found that the absorption transition character can be altered by changing the electron-withdrawing groups. These results indicate that absorption properties are governed by the HOMO-LUMO energy gap and consequently there is a large shift towards the lower energies in the absorption bands (bathochromic effect). The addition of more substituents causes a blue shift of the absorption band (hypsochromic effect) compared to mono substituted compounds.

**Keywords:** electronic spectra, HOMO-LUMO gap, bathochromic effect, electron-withdrawing

**Résumé**

Une étude théorique basée sur la théorie fonctionnelle de la densité (DFT) a été réalisée sur acide benzofurane-2-carboxylique et ses dérivés comprenant les substituants OH, Cl, NH<sub>2</sub> et CH<sub>3</sub>. L'optimisation géométrique et les propriétés électroniques ont été étudiées en utilisant la méthode BP86/TZP. Les résultats révèlent que les groupes électroattracteurs n'ont qu'un effet mineur sur les paramètres géométriques et diminuent les écarts énergétiques HOMO-LUMO. Au moyen de la méthode TD-DFT, les spectres d'absorption ont été calculés sur la base des géométries optimisées de l'état fondamental. On constate que le caractère de transition d'absorption peut être modifié en changeant les groupes électroattracteurs. Ces résultats indiquent que les propriétés d'absorption sont régies par l'écart énergétique HOMO-LUMO et par conséquent, il y a un grand déplacement vers les énergies plus basses dans les bandes d'absorption (effet bathochrome). L'ajout de plus de substituants provoque un déplacement vers le bleu de la bande d'absorption (effet hypsochrome) par rapport aux composés mono substitués..

**Mots clés :** spectre électronique, HOMO-LUMO gap, effet bathochrome, électro-attracteur

**ملخص:**

تم إجراء دراسة نظرية تعتمد على نظرية الكثافة الوظيفية DFT على حمض بنزوفيران -2 كربوكسيليك ومشتقاته بما في ذلك المستبدلات OH, Cl, NH<sub>2</sub>, CH<sub>3</sub> تم فحص التحسين الهيكلي والخصائص الإلكترونية باستخدام BP86/TZP كشفت النتائج أن مجموعات سحب الإلكترون ليس لها سوى تأثير طفيف على الخصائص الهندسية وتعمل على إنقاص قيم الفجوات HOMO-LUMO باستخدام طريقة TD-DFT تم حساب أطياف الامتصاص اعتمادا على الحالات الهندسية المستقرة.

يمكن ملاحظة أنه يمكن تعديل طابع انتقال الامتصاص عن طريق تغيير مجموعات سحب الإلكترون. تشير هذه النتائج إلى أن خصائص الامتصاص تحكمها فجوة طاقة HOMO-LUMO. وبالتالي هناك تحول كبير نحو الطاقات المنخفضة في نطاقات الامتصاص (تأثير باتو كروم). تؤدي إضافة المزيد من البدائل إلى حدوث تحول نحو أزرق في نطاق الامتصاص مقارنة بالمركبات أحادية الاستبدال (تأثير ايبسوكروم)

**كلمات مفتاحية:**

طيف الكتروني، الفجوة الطاقوية HOMO-LUMO ، تأثير باتو كروم، ساحة للإلكترونات