Time dependent density functional study of the absorption spectra of 1,3-benzoxazole and three substituted benzoxazole in gas phase and liquid phase

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Abstract: Time dependent density functional (TD-DFT) calculations were performed on 1,3-benzoxazole and substituted benzoxazoles using the B3LYP functional and the 6-31+G(d) basis sets. The geometry of the S₀ and S₁ singlet ground and excited states were optimized in gas phase, toluene and methanol using B3LYP/6-31+G(d) y CIS/6-31+G(d) methods, respectively, and the vertical π → π* absorption largest wavelength transitions were determined. Several global molecular descriptors were considered such as the hardness, chemical potential, electronegativity and the dipole moment for each molecule and was determined the influence that has, about the values of these descriptors, the alteration of the main molecular chain of an initial structure (1,3 not substituted Benzoxazole). Generally, the predicted spectra are in agreement with the experimental data.

Key words: benzoxazole, Gaussian, absorption and the Density Functional Theory.

1. Introduction

The benzoxazole's family (1,3-benzoxazole and its derivatives) constitute one of the main groups of organic fluorescent materials. They have been studied due to their interesting spectroscopic and photophysical properties [1, 2]. This kind of molecule shows fluorescent emission with a large Stokes shift that originates from an intramolecular proton-transfer reaction in the electronic excited state [3-5]. This phenomenon has widespread implications in the action of many lasing dyes, photostabilizers, well as research in physics, chemistry [6-8], technological applications [5] and its use in medicine [4] and biology [9]. From the point of view of its photophysical properties, the benzoxazoles derivatives have been much studied as components of organic dye laser systems [10, 11] where our main interest on these compounds lies, and fluorescent probes [12].

On the other hand, a common problem for both the spectroscopy and laser physics is known in the literature as: "The first fundamental problem of common interest for Optical Spectroscopy and Laser Physics", which is related with the search of actives medium for tunable lasers based on dyes, thereby seeking the greatest coverage of the spectral band with the laser effect [1, 2, 13, 14].

Once you try to find a solution to this problem, in the proposals reported by the literature is the use of three-ring compounds and more complex structures that contain such fragments. Among those structures are included some derivatives of the benzoxazole, since has been experimentally demonstrated in some of these good properties of absorption, fluorescence and laser effect [6, 7].

On the other hand, we know that the proper alteration of a molecular structure initial (parent structure), in many cases has allowed to obtain the laser effect in other regions of interest of optical spectral. All this shows how it is possible to go covering different spectral regions and expand more and more spectral coverage with the laser effect using dyes as active medium [8].
All in all, it was done in this paper a theoretical study of the electronic properties of the 1,3-Benzoazole and three derivative molecules. Calculations were performed mainly in three steps. Geometry optimization of the molecules in the ground state was performed at the DFT/6-31+G(d) level, using B3LYP functional. These calculations were followed by a determination of the Hessian to assess whether the stationary points obtained were minima and to obtain the vibrational spectra of the molecules. The second step consisted in a TDDFT calculation of the absorption spectrum of the molecules. Normally up to 20 singlet excited states were included in the calculations but only the one or two lowest states were included in the discussion. Finally, the third step consisted in the geometry optimization of the chosen excited state obtained. Then, were calculated several molecular descriptors like: molecular hardness ($\eta$), energy gap (energy difference between first ionization potential and the electronic affinity), first ionization potential ($I$), the electronic affinity ($A$) and the dipolar moment. The hardness was calculated by the formula:

$$\eta = \frac{1}{2}(I - A)$$

Where $I = E(N-1) - E(N)$, it is the first ionization potential - energy difference between cation and molecule on the base of the optimized structure of neutral molecule- and $A = E(N+1) - E(N)$, it is the electronic affinity - energy difference between anion molecule on the base of the optimized structure of neutral molecule-.

Finally, we extend the study to some substituted benoxazoles, not yet included in previous works, in order to obtain conclusions about the effect of substituents in the red shift of the absorption bands of benoxazoles. The 1,3-Benzoxazole and derivative structures with R-substituent are shown in Table 1 and Fig. 1.

| MOLECULAR STRUCTURES       | R       |
|---------------------------|---------|
| I: 1,3-Benzoxazole        | H       |
| II: 2-Phenyl-1,3-Benzoxazole | C6H5   |
| III: 2-Orto-Fluor-Phenyl-1,3-Benzoxazole | C6H4F |
| IV: 2-Orto-Cloro-Phenyl-1,3-Benzoxazole | C6H4Cl |

Table 1. 1,3-Benzoxazole and derivatives.

![Figure 1. Structures of 1,3-benoxazole and derivatives](image-url)
3. Methodology and Computational Details

Quantum chemical calculations were carried out using the Gaussian 03 program \cite{15} package. Geometrical optimizations of the ground states were done using RB3LYP method with 6-31+G(d) basis set. The geometries of the first singlet excited state in gas phase were optimized using the configuration interaction singles (CIS) method with 6-31+G(d) basis set. On the basis of optimized structures for the ground state, TD-DFT method with 6-31+G(d) basis sets were used to predict the absorption wavelengths. In the TD-DFT calculations the RB3LYP functions were used. The solvent effect on spectrum was considered using the PCM model \cite{16}. The solvents used in our calculations were methanol (dipolar moment: 1.69 Debye and dielectric constant: 33) and toluene (dipolar moment: 0.36 Debye and dielectric constant: 2.4). So that, the methanol is considerate polar solvent while the toluene nonpolar solvent. The UV-Vis spectra were plotted using the GausSum 2.2.Ob computer program.

4. Results and discussion

4.1 Geometries and charges of the ground states

The ground state geometries of 1,3-Benzoxazole (structure I) optimized with RB3LYP/6-31+G(d) method in gas phase and liquid phase are shown in Fig. 2 and the serial numbers of atoms are also indicated. The bond lengths of structures II, III and IV are shown in Table 2. Only a few bond lengths for each structure are shown. The ground state exhibits for each structure an almost completely planar configuration with alternating, delocalized $\pi$ bonding on benzene like it shown the torsion angle of 180 degrees in Fig. 2 and 3.

A comparison of some relevant geometrical parameters of the three studied benzoxazoles among themselves and with respect to the 1,3-benzoxazole parent specie I are reported in Table 2 and in Fig. 2 and 3. The most noticeable aspect of the structure of R-phenyl substituted benzoxazole is the co-planarity of the benzoxazole skeleton and the benzene substituent. For instance, the two planes exhibit a dihedral angle of about 180 degrees for the ground state of each structure in gas phase, keeping this co-planarity in liquid phase.

Otherwise, and as shown in Fig. 2, the O-C bonds are almost equal of about 1.37 Å and there is a clear (C-N=C) alternating single and double bond configuration around N. Being the C2-N bonds shorter than the length of a normal N-C single bond (1.47 Å) and longer than the length of a normal N=C double bond (1.30 Å). It indicates that bonds C2-N of 1,3-benzoxazole compounds have partly the characteristic of double bond. While than the N-C7 bond coincides with the length of a normal N=C double bond of 1.30 Å.

The effect of the solvent, as appreciated in Fig. 2 is also almost negligible and in the direction that was expected because of the electrostatic stabilization of the dipole moment. The Mulliken Charges calculated for each atom (only shown the major atoms) are shown in Table 3. One can see that the solvent polarizes the charges in the expected direction for a polar solvent, increasing the charge transfer from the benzene fragment to the oxazole ring. The same effect is of course observed in the dipole moment (shown in Table 7), which increases once the continuum dielectric representing methanol is included.

On the other hand, the Fig. 3 shown the effect of the phenyl substituted in the structure I, the phenyl group has little effect on nitrogen and oxygen atoms. Specifically, the negative charge on nitrogen atom is decrease, while the negative charges on the oxygen atom and carbon atoms near them are increase. The chlorine and fluorine atoms substituted in phenyl group causes the decrease the negative charges in oxygen and nitrogen atoms, in greater proportion with the chlorine atom than with the fluorine atom. It is attributed to the electron-attracting effect of fluorine and chlorine atoms.
Table 2. Bond lengths (Å) in gas phase and liquid phase for the ground state of structures II, III and IV optimized with RB3LYP/6-31+G(d) methods.

| BONDS | II (GAS) | II (MET) | II (TOL) | III (GAS) | III (MET) | III (TOL) | IV (GAS) | IV (MET) | IV (TOL) |
|-------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| C1=C2| 1.403   | 1.402   | 1.402   | 1.402   | 1.401   | 1.402   | 1.402   | 1.401   | 1.402   |
| C2-C3| 1.399   | 1.400   | 1.399   | 1.400   | 1.401   | 1.400   | 1.400   | 1.400   | 1.400   |
| C3=C4| 1.396   | 1.398   | 1.397   | 1.395   | 1.397   | 1.395   | 1.395   | 1.397   | 1.396   |
| C4=C5| 1.409   | 1.411   | 1.410   | 1.410   | 1.412   | 1.410   | 1.410   | 1.411   | 1.411   |
| C5=C6| 1.399   | 1.401   | 1.400   | 1.398   | 1.400   | 1.398   | 1.399   | 1.400   | 1.399   |
| C1=C6| 1.387   | 1.387   | 1.387   | 1.388   | 1.388   | 1.388   | 1.387   | 1.388   | 1.388   |
| C1-O | 1.374   | 1.375   | 1.374   | 1.372   | 1.375   | 1.372   | 1.373   | 1.375   | 1.374   |
| O-C7 | 1.382   | 1.379   | 1.381   | 1.375   | 1.373   | 1.375   | 1.376   | 1.376   | 1.376   |
| C2-N | 1.382   | 1.395   | 1.393   | 1.389   | 1.392   | 1.389   | 1.390   | 1.393   | 1.392   |
| N=C7 | 1.301   | 1.304   | 1.302   | 1.305   | 1.307   | 1.304   | 1.303   | 1.305   | 1.304   |
| C7-C14| 1.460  | 1.461   | 1.461   | 1.467   | 1.468   | 1.467   | 1.462   | 1.462   | 1.462   |
| C14=C15| 1.406  | 1.408   | 1.407   | 1.413   | 1.414   | 1.412   | 1.411   | 1.412   | 1.411   |
| C15=C17| 1.393  | 1.394   | 1.393   | 1.388   | 1.389   | 1.389   | 1.390   | 1.391   | 1.391   |
| C17=C21| 1.400  | 1.401   | 1.400   | 1.398   | 1.399   | 1.398   | 1.400   | 1.401   | 1.401   |
| C21=C19| 1.398  | 1.399   | 1.399   | 1.392   | 1.394   | 1.393   | 1.394   | 1.396   | 1.395   |
| C14=C16| 1.405  | 1.407   | 1.406   | 1.411   | 1.411   | 1.411   | 1.403   | 1.403   | 1.403   |
| C16=C19| 1.395  | 1.396   | 1.396   | 1.399   | 1.398   | 1.398   | 1.390   | 1.389   | 1.388   |
| C16-H20| 1.085  | 1.088   | 1.086   |         |         |         |         |         |         |
| C16-CL| 1.756   | 1.763   | 1.756   |         |         |         |         |         |         |
| C16-F | 1.354   | 1.361   | 1.357   |         |         |         |         |         |         |

Figure 2. The ground state structures of 1,3-Benzoxazole optimized with RB3LYP/6-31+G(d) method.

4.2 Electronic structures of the ground states

Molecular Orbital (MO) calculations were performed on the base of the geometrical structures optimized by B3LYP/6-31+G(d) method. Shapes and types of molecular orbitals (MOs) of each structure were presented in Fig. 4. The lowest unoccupied molecular orbital (LUMO) and the second unoccupied molecular orbital (LUMO+1) of four compounds are π*-type MO. The highest occupied molecular orbital (HOMO) and the second occupied molecular orbital (HOMO-1) of four compounds are π-type MO. The third occupied molecular orbital (HOMO-2) of 1,3-benzoxazole is n-type MO (low transition probability). While, the third unoccupied molecular orbital (LUMO+2) of 1,3-benzoxazole is Rydberg-type MO.
Different orbital energies and HOMO–LUMO energy gaps of the four benzoxazole compounds are presented in Table 4. As shown in Table 4, phenyl substituted in R-position of 1,3-Benzoxazole raise negative energies of the unoccupied orbitals (LUMO, LUMO+1 and LUMO+2) and lower negative energies of the occupied orbitals (HOMO, HOMO-1 and HOMO-2). So the difference of energy between HOMO and LUMO is reduced, and the transition from HOMO to LUMO becomes easier for structure II that for structure I. The halogens substituted in phenyl group also makes the transition from HOMO to LUMO easier because the energy gap of the compounds III and IV is lower than that of structure II. This implies an increase in the electro-acceptor capacity of the structure as a consequence of altered its main molecular chain.

| ATOMS | GAS | MET | TOL | GAS | MET | TOL | GAS | MET | TOL | GAS | MET | TOL |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C1    | 0.599 | 0.681 | 0.637 | 0.643 | 0.655 | 0.655 | 0.786 | 0.821 | 0.803 | 0.710 | 0.745 | 0.727 |
| C2    | 0.891 | 1.046 | 0.962 | 0.434 | 0.504 | 0.467 | 0.473 | 0.544 | 0.504 | 0.496 | 0.579 | 0.534 |
| N     | -0.342 | -0.444 | -0.387 | -0.308 | -0.407 | -0.349 | -0.288 | -0.376 | -0.325 | -0.290 | -0.380 | -0.329 |
| O     | -0.327 | -0.340 | -0.334 | -0.388 | -0.398 | -0.393 | -0.351 | -0.375 | -0.366 | -0.379 | -0.396 | -0.386 |
| C7    | 0.326 | 0.337 | 0.331 | 0.574 | 0.639 | 0.599 | 0.181 | 0.231 | 0.201 | 0.824 | 0.863 | 0.839 |
| C14   | 0.434 | 0.440 | 0.441 | -0.842 | -0.780 | -0.815 | 0.398 | 0.433 | 0.415 |
| C16   | -0.332 | -0.371 | -0.348 | 1.123 | 1.032 | 1.083 | 0.220 | 0.244 | 0.222 |
| C19   | -0.390 | -0.446 | -0.416 | -0.450 | -0.460 | -0.452 | -0.186 | -0.269 | -0.223 |
| H20   | 0.208 | 0.289 | 0.220 | 0.295 | 0.259 | 0.278 | 0.295 | 0.259 | 0.278 |
| Cl    | -0.335 | -0.359 | -0.346 |
| Fl    | -0.335 | -0.359 | -0.346 |

Table 3. Mulliken charges (e) in gas phase and liquid phase for the ground state of each structure obtained with RB3LYP/6-31+G(d) method.

Figure 3. The ground state structures of compounds II, III and IV optimized with RB3LYP/6-31+G(d) method.
Figure 4. The plots of the frontier molecular orbital of compounds I, II, III and IV obtained by B3LYP/6-31+G(d) method.

Table 4. Energies (eV) of Frontier Molecular Orbitals in gas phase obtained by B3LYP/6-31+G(d) method.

| ORBITAL | I  | II  | III | IV  |
|---------|----|-----|-----|-----|
| LUMO+2  | 0.163 | -0.381 | -0.435 | -0.408 |
| LUMO+1  | -0.299 | -0.626 | -0.871 | -0.707 |
| LUMO    | -1.170 | -1.769 | -1.959 | -1.905 |
| HOMO    | -6.857 | -6.286 | -6.367 | -6.367 |
| HOMO-1  | -7.048 | -6.912 | -6.966 | -6.939 |
| HOMO-2  | -8.327 | -7.293 | -7.156 | -7.293 |
| GAP     | 5.687 | 4.517 | 4.408 | 4.462 |

4.3 Molecular Descriptors

The Ionization potential indicates the ability of losing electron and the electronic affinity indicates the ability of gaining electron. The Table 5 lists the calculated ionization potentials (I) and electronic affinity (A) of the four compounds, using RB3LYP/6-31+G(d) level. Was calculated the vertical ionization potential, which denotes the energy difference between cation and molecule on the base of the optimized structure of neutral molecule. From the data we can see that the vertical ionization
potential of each structure is decreased and the electronic affinity is increased, i.e. the ability of losing electron is reduced for each compound gradually. This means derivatives structures can act as good electron-acceptor materials, increasing these properties more and more in liquid phase.

Table 5. Ionization potential and electronic affinity of each Structure, using RB3LYP/6-31+G(d) level.

| Structure | Gas | Methanol | Toluene |
|-----------|-----|----------|---------|
| I         | I   | A        | I       |
|           | 8.90| -0.60    | 6.79    |
| II        |     |          |         |
|           | 8.10| -0.04    | 6.23    |
| III       |     |          |         |
|           | 7.95| 0.49     | 6.30    |
| IV        |     |          |         |
|           | 8.17| 0.06     | 6.31    |

The Table 6 lists the calculated total energy of each compound, from the data we can see that each Structure is more stable in liquid phase than that in gas phase (greater negative energy), this stability being a few higher in methanol than in toluene.

Table 6. Comparison of total energy and molecular hardness of each Structure in gas phase and liquid phase obtained with RB3LYP/6-31+G(d) method.

| Structure | Total Energy (Hartree) | Molecular Hardness (eV) |
|-----------|------------------------|-------------------------|
|           | Gas        | Methanol   | Toluene | Gas  | Mot. | Tol. |
| I         | -399.738   | -399.745   | -399.740| 4.75 | 2.74 | 3.56 |
| II        | -630.812   | -630.825   | -630.818| 4.07 | 2.12 | 2.81 |
| III       | -730.044   | -730.055   | -730.048| 3.73 | 2.07 | 2.76 |
| IV        | -1090.398  | -1090.405  | -1090.401| 4.05 | 2.11 | 2.80 |

Table 7. Dipolar moment of each Structure in gas phase and liquid phase for ground state and first excited state.

| Structure | Dipolar Moment (Debye) |
|-----------|------------------------|
|           | Gas | Excited | Methanol | Ground | Excited | Toluene | Ground | Excited |
| I         | 1.399 | 2.685 | 2.054 | 3.613 |
| II        | 1.164 | 6.645 | 1.857 | 6.023 |
| III       | 0.718 | 7.440 | 1.067 | 6.500 |
| IV        | 0.924 | 8.042 | 1.333 | 6.483 |

The Table 6 lists the calculated hardness of each structure in gas phase and liquid phase. The molecular hardness gives an approximation of the reactivity of a molecular system through the "principle of maximum hardness" [17], where it has established that more reactive systems have a low hardness and less reactive systems have a high hardness. The molecular hardness is a very stable property, and it is very convenient to classify the intrinsic reactivity of molecular systems studied. So you can see (Table 6) that the parent structure presents the lower reactivity both in vacuum like in liquid phase, while the compound III has the highest reactivity.
4.4 UV absorption spectra

The changes observed in the absorption spectra are collected in Table 8. Substitution of the hydrogen in R by a phenyl group red-shifts the absorption by about 50 nm. The halogen substituent in the ortho position of the substituent phenyl group acts as a small perturbation in the same direction, increasing again the wavelength of the transition. The same effect is noticed in gas phase and in the solvents, only that the effect of the halogen substituent is more noticeable in liquid phase than in the gas phase. A further effect of the phenyl substituent is noticed: the oscillator strengths are much larger than those in the parent molecule. The whole transition is basically a charge transfer from the benzene to the oxazol rings (as can be seen in Table 9).

The superposition of the absorption spectra of each structure in gas phase is shown in Fig.5. The UV absorption spectra of 1,3-Benzoxazole and 2-Phenyl-1,3-Benzoxazole were obtained from literature \[11\]. The experimental data were compared with the calculated data by TD-B3LYP/6-31+G(d) methods. The comparisons of results of the lowest excitation energies, oscillator strengths and the peaks with the largest wavelength (\(\lambda_{\text{max}}\)) are shown in Table 8. There are 30-40 nm differences between the calculated \(\lambda_{\text{max}}\) and the experimental \(\lambda_{\text{max}}\) obtained from literature \[18\] for I and II structures.

![Figure 5](image)

**Figure 5.** Comparison absorption spectra of each Structure in gas phase obtained with TD-B3LYP/6-31+G(d) level.

The calculations above-mentioned are all in gas phase, not in solvent. The experimental data were obtained in ACN. So the calculations by TD-DFT in solvent were done using PCM model. The results are also listed in Table 8 and they will be discussed later. As shown in Table 8, the maximal absorption wavelengths of II-structure are red-shifted compared with those of I-structure which is because that the substitution of hydrogen atom in R-position by the phenyl group in II-structure has a better electron delocalization than that in I-structure. And the maximal absorption wavelengths of III and IV structures are red-shifted compared with those of II-structure which is because of the substitution of one hydrogen atom in the phenyl group by one chlorine and fluorine atom in III and IV structures. However, it’s clear that with the halogen substituent, the absorption band suffers a large
hypochromic effect, i.e., a decrease in both the intensity of the absorption band and the probability of transition.

The superposition of the absorption spectra obtained in gas phase, toluene and methanol (only the structure IV is shown) are shown in Fig. 6. The image in Fig. 6 and the data in Table 8 show that there is an important effect of the solvent. All transitions are red shifted (bathochromic effect) when the solvent is present, as well as when the polarity of the solvent increases and makes the calculated values nearer to the experimental data. At the same time, the solvent produces in absorption band a large hyperchromic effect, i.e., an increase in both the intensity of the absorption band and the probability of transition.

| Structure | Excitation Energies (eV) | Absorption Wavelength (nm) | f |
|-----------|--------------------------|---------------------------|---|
|           | Gas | Met. | Tol. | Gas | Met. | Tol. | Gas | Met. | Tol. |
| I         | 5.05 | 5.04 | 5.03 | 242.33 | 243.95 | 246.54 | 0.045 | 0.071 | 0.084 |
| II        | 4.20 | 4.10 | 4.07 | 295.41 | 302.50 | 304.79 | 0.741 | 0.872 | 0.927 |
| III       | 4.09 | 4.01 | 3.97 | 303.26 | 309.39 | 312.14 | 0.673 | 0.812 | 0.857 |
| IV        | 4.14 | 4.07 | 4.03 | 299.50 | 304.97 | 308.00 | 0.700 | 0.849 | 0.893 |

Table 8. Changes in the absorption spectra of each molecular system in gas phase and liquid phase obtained with TD-B3LYP/6-31+G(d) level.

Figure 6. Effect of the solvent in the spectra absorption of the 2-Orto-Flúor-Phenyl-1,3-Benzoxazole, using TD-RDFT/B3LYP/6-31+G(d) method and PCM model.

4.5 Geometries and electron distribution of the first excited states

The geometries of the first excited state were optimized at the CIS/6-31+G(d) level of theory. The optimized geometrical parameters for I, II, III and IV structures in gas phase are listed in Fig. 7 and the
serial numbers of atoms are also indicated. In all compounds, the torsion angles of C3-C2-N-C7 are 180°, which Geometry optimization of the excited state keeping the planar structure of the ground state. As shown in Fig. 7, the bond lengths of both of bonds C1-O and O-C7 are shorter than those of the ground states in I and II structures, while a little longer in III and IV structures. The lowest singlet transitions for the four compounds are the transition from the HOMO to LUMO (\(\pi \rightarrow \pi^*\) transitions), so the change of bond length can be understood by analyzing the HOMO and LUMO orbitals. There is smaller density on the C1-O and O-C7 bond for the HOMO, but the electron density for the LUMO increases. So the bond length of these bonds decreases. The longer of these bonds in III and IV structures can also be interpreted in terms of the patterns of HOMO and LUMO.

These differences in bond lengths between the ground state and first excited state, can be interpreted by the charge redistribution (measured by Mulliken) of each atom in the structure for go from ground state to the excited state. For example, the O goes from -0.327 to -0.453, while N changes from -0.342 to -0.369; these changes in gas phase are shown in Table 9, showing the same difference in liquid phase only than that in a higher proportion.

### Table 9. Electron distribution comparisons in gas phase of the ground state and the first excited state.

| Atoms | I       | II      | III     | IV      |
|-------|---------|---------|---------|---------|
|       | Groun. | Exc.    | Groun.  | Exc.    |
| C1    | 0.399  | 0.323   | 0.643   | 0.392   |
| C2    | 0.891  | 0.221   | 0.434   | 0.266   |
| N     | -0.342 | -0.369  | -0.308  | -0.308  |
| O     | -0.327 | -0.453  | -0.338  | -0.514  |
| C7    | 0.326  | 0.377   | 0.574   | 0.321   |
| C14   | 0.434  | 0.513   | 0.842   | 0.271   |
| C16   | -0.332 | -0.220  | 1.123   | -0.266  |
| C19   | -0.390 | -0.459  | -0.450  | -0.192  |
| H2O   | 0.208  | 0.270   |         |         |
| F     |         |         | 0.295   | -0.039  |
|       |         |         | -0.335  | -0.331  |

**Figure 7.** The excited state structures of compounds I, II, III and IV in gas phase optimized with CIS/6-31+G(d) method.
5. Conclusions

We have performed DFT and TD-DFT calculations of the structure of the S0 and S1 states of several benzoxazoles, including the parent structure. We have found that substitution of the benzoxazole skeleton affects the absorption spectrum, mainly through the modification of the structure of the excited states. In the cases where a substituent capable of delocalization was placed at R-position of the parent structure, we found that excitation from coplanar ground states produces absorption at longer wavelengths. Important solvatochromic effects of the same magnitude than those observed experimentally were obtained from the calculations. It was additionally shown that a relatively small 6-31+G(d) basis set was enough to obtain excellent results for absorption spectra at the TD-DFT level, provided that solvation effects were included at least at the level of the PCM methodology. In a pair of cases studied however, data suggest that specific solvation effect may be playing their role.

The results show that the halogen substituent used produce (as can be seen in fig. 8 and Table 7) a good increase in the difference between the ground state dipole moments with respect to the excited states, which facilitates the transport of charge through the main molecular chain, this implies than the derivatives structures increase their electronic properties compared to those of the parent structure.

![Figure 8](image.png)

**Figure 8.** Comparison of the dipolar moment of ground state and of the excited state in gas phase.

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