Theoretical description of the electronic properties and intrinsic chemical reactivity of organic compounds derived from 1,3-Benzoxazole

E S Rivera¹, O I Ávila¹, and O L Neira¹
¹ Grupo de Espectroscopia Óptica y Láser, Universidad Popular del Cesar, Valledupar, Colombia

E-mail: oscarneira@unicesar.edu.co

Abstract. The electronic and intrinsic chemical reactivity properties of four single ring chain structure organic compounds derived from 1,3-Benzoxazole, based on to mono- and bi-substitution of acceptor and donor fragments of electrons. This theoretical study was motivated by the need to inquire specifically about the effect of electric charge transfer individual and simultaneous of the substitutes into one of the parent compound phenyl rings. The amino and nitro groups were used as fragments, respectively. The results found from this study are important because it provides key aspects to understand mechanisms for the design of novel structures for the development of new materials with appropriate properties and explore their potential use as biomarkers, active media for tunable lasers, or active layers for solar cells and suggest their possible use for these applications based on 27-Phenyl-30-Oxazol-2-Phenyl-1,3-Benzoxazole from the comparative study of their electronic and chemical reactivity properties of 27-Phenyl-30-Oxazol-2-Phenyl-1,3-Benzoxazole and compounds derived. The Gaussian 03 software suite was used as a computer calculation tool, while the calculations were computed by using the hybrid functional that combines Becke's three-parameter exchange functional with Lee Yang Purr's correlation functional.

1. Introduction
Organic molecules with pi-conjugated bonds have been highly relevant in recent decades due to their interesting optical and electronic properties [1,2], [3-14], therefore, the organic compounds (COs) formed from said molecules have a set of applications such as the creation of organic light-emitting diodes (OLED) [3,12], tunable lasers [6,15,16], organic field effect transistors (OFET) [3,12] and organic photovoltaic (OPV) [5,17,18]. That is, this type of COs plays an important role; since its potential use is related and depends on the optical, electronic, optoelectronic and photostability properties of the substances used for each specific purpose [1,8,15,19-26]. On the other hand, in medicine and biology the use of fluorescent compounds as biomarkers or dynamic phototherapy is very important for diagnosis [27,28]. Oxazole and oxadiazole belong to the class of five-membered heterocyclic rings that include nitrogen and oxygen atoms, separated by a carbon atom. It is known from literature reports that oxazol derivatives with three and four single alternating ring chain structure possess intense absorption and fluorescence in the optical spectrum [17,18], being used to develop photodetectors in ultraviolet and fluorescence microscopy applications respectively. The laser effect has been achieved in some compounds with molecular structures of four or five simple monocyclic rings alternating with oxazol (oxadiazole) with phenyl [17,18]. Due to the presence of oxygen and nitrogen...
with isolated non-binding electron pairs at the vertices of the ring of which they are part, contributing by means of resonance to the effect of charge transfer to the molecular system, so they can be used in electron transport materials for the development of optical devices such as the active layer of an organic photodiode or a solar cell [5]. On the other hand, pi conjugated electrons from oxadiazole derivatives open the possibility of developing non-linear optical materials [6].

In this context, the electronic properties and intrinsic chemical reactivity have been designed and modeled of four. The positions chosen were respectively the ortho-position and the para position of the phenyl ring of the extreme position of the molecular chain (see Table 1). A comparative study was made of the electronic properties and chemical reactivity of 27-Phenyl-30-Oxazol-2-Phenyl-30-Oxazol-2-Phenyl-1,3-Benzoxazole with the three derived structures. The results obtained from the research are important for the interpretation of the behavior of the compound studied in terms of its electronic properties and intrinsic chemical reactivity, based on global molecular descriptors such as the energy of the border orbitals, the energy gap; vital information for the second phase of research, where all that information is necessary to identify absorption and emission centers in the study of the optical properties of absorption and fluorescence on its potential use as an active medium for tunable lasers or active layers for solar cells.

### Table 1. Molecular structures under study.

| I          | 27-Phenyl-30-Oxazol-2-Phenyl-1,3-Benzoxazole |
|------------|--------------------------------------------|
| II         | 40-Orthoammonia-27-Phenyl-30-Oxazol-2-Phenyl-1,3-Benzoxazole |
| III        | 32-Paranitro-27-Phenyl-30-Oxazol-2-Phenyl-1,3-Benzoxazole |
| IV         | 40-Orthoammonia-32-Paranitro-27-Phenyl-30-Oxazol-2-Phenyl-1,3-Benzoxazole |

#### 2. Theoretical foundations and computational details

The prediction or modelling of the electronic, reactivity and selectivity properties of a molecular system, is key and critical respectively, to understand the optical properties of organic materials and the optical processes that occur in molecules that constitute them. On the other hand, there are different approaches with their theories, which have been proposed to explain these properties. Each theory proposes its own set of local and global indices of reactivity and selectivity to describe either physical processes in a molecular system or chemical processes. Global indices such as electronegativity and hardness have been introduced to characterize the reactivity of a compound.

On the other hand, one of the great advances of the theory of density functions from its conceptual part, has allowed the union, arrangement and unification of most of the local and global descriptors of the systems of interest in a single and unique theory. The Kohn-Sham potential energy in the density functional theory, i.e. the total energy of the system (energy of the fundamental state of an atom or molecule) E is expressed as a functional of the electron density \( \rho(r) \) as shown by Equation (1), in the form [21,22].

\[
E[\rho(\vec{r})] = F[\rho(\vec{r})] + \int_{\tau} v(\vec{r})\rho(\vec{r}) \, d\tau, \tag{1}
\]

where \( v(\vec{r}) \) is the external potential acting on the interacting system (at minimum, for the molecular system, the electron-nuclear interaction) and \( F \) is the universal Hohenberg-Kohn functional. On the other hand, from the definitions of the chemical potential \( \mu \) and hardness \( \eta \) given by Parr and Pearson [23,24] and using the approximation of finite differences for three points for hardness and two points for...
chemical potential, and using the Koopmans theorem, the energies of the orbital boundaries Homo and Lumo orbital limits are finally obtained from Equation (2) and Equation (3).

\[ \mu = \frac{1}{2}(\varepsilon_L + \varepsilon_H), \]  \tag{2}

\[ \eta = \frac{1}{2}(\varepsilon_L + \varepsilon_H). \]  \tag{3}

Taking into account how important the characterization in the ground state in the gas phase is for the molecular structures under study, then, when doing the optimization calculation by the computational algorithms, it is possible to obtain the information related to the intrinsic chemical reactivity, that is, how the 1,3-Benzoxazole molecule is predisposed to react when it has molecules around it and this is done in terms of characteristics of what are known as global and local molecular descriptors. With the help of the GaussView 5.0 program, which provides us with a graphical interface, the molecular structures of interest were designed and visualized (see Table 1).

Then, as what was intended is to be able to obtain a characterization from the electronic properties and intrinsic chemical reactivity of the 4 molecules under study, such as: the energy value, the dipole moment, the energy gap, the homo and lumo boundary orbitals, the electronegativity, the molecular hardness, the transition wavelength, the spectral frequency and the spectral shift achieved.

For this, the stationary density functional theory (DFT) approach was used [2,15,18,24-32], with the functional Lee-Yang-Parr hybrid of three parameters B3LYP [15,20,21,32] and the base functions 6-31+G(d) [20,32]. For this, a SUPERMICRO AS-4042G-6RF server was used, which has 32 cores and 320 MW, the Gaussian 03 software package suite was used as computational calculation tools.

3. Results obtained and interpretation
In accordance with the importance of the modeling of electronic properties and intrinsic chemical reactivity within the different branches of science [1,11,19,21,32], the results obtained and the discussion of these are presented.

3.1. Interpretation for the obtained energy values
Table 2 shows the computational results for the molecular structures under study; dentro de las cuales se destaca la molécula I (27-Fenil-30-Oxazol-2-Fenil-1,3-Benzoxazol), because this is the mother molecular structure, whose energy value was calculated in -30116.91 eV. For molecule II it was -31447.82 eV, which means that the energy of molecule II decreased 4.42% than the energy of the mother molecule. For molecular structure III it was -35482.84 eV, implies that the energy of molecule III decreased 17.82% higher than the energy of the mother molecule, in addition, higher than the derived molecule II. For molecular structure IV (40-Ortoamoniacaco-32-Paranitro-27-Fenil-30-Oxazol-2-Fenil-1,3-Benzoxazol) the total energy is -36981.15 eV, therefore, it decreased by 22.79% compared to the energy of the parent molecular structure. The results of the energy of each of the derived molecular structures, it can be seen that in all cases the value of energy decreased compared to the parent molecular structure, the one with the lowest energy is molecule IV, and the one with the highest energy is molecule II.

By highlighting the influence of the amino (-NH₂) group in the ortho position for molecule II and the nitro group (NO₂) in the para position of molecule III, and both substitutions in the derived molecule IV, make the total energy is much greater than the total energy of the mother molecule and the other derivatives under study [1,15,16,23].

3.2. Interpretation of the dipole moment
The dipole moment is an electronic property, which gives a measure of the asymmetry of the charge distribution inside the molecule [1,5,33], therefore the measure of the intermediate intensity of the attractive force between the atoms. In the case of the mother molecule it is 2.33 D. For the derived

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molecular structure II (see Table 1), the calculated dipole moment is 3.72 D, corresponding to a 59.66% increase compared to the dipole moment of the parent molecular structure. For molecule II it was 6.01 D, that is, its dipole moment increased by 157.94% compared to that of the parent structure. It can be seen that molecule III has a higher dipole moment compared to molecule II, this is due to the influence of the nitro group on the derived molecule III that allows the mobility of electrons from the primary block to the nitro electron acceptor fragment, contrary case to what happens with the derived molecule II that owning an amino fragment, the distribution of electrons is made such that it receives electrons from the donor amino group.

Furthermore, for molecule IV, the dipole moment was 8.90 D, it increased by 281.97% compared to the dipole moment of the mother molecule. Likewise, if it is compared with the other results of the dipole moment for the molecular structures studied, the increase is notorious. This implies that when the Push-pull effect occurs thanks to the simultaneous influence of the donor -NH2 group with a fragment in the ortho position, and the -NO2 acceptor group with a fragment in the para position, in the considered increase in the dipole moment of the IV derived molecule compared to the other molecular structures under study, as suggested by J Y Lai (2012) [34].

| Molecular descriptors | I       | II      | III     | IV      |
|-----------------------|---------|---------|---------|---------|
| Energy (eV)           | -30116.91 | -31447.82 | -35482.84 | -36981.15 |
| Dipole moment (Debye) | 2.33    | 3.72    | 6.01    | 8.90    |
| Homo (eV)             | -5.96   | -5.31   | -6.09   | -5.96   |
| Lumo (eV)             | -1.98   | -1.70   | -2.78   | -2.17   |
| Energy gap ΔE_gap (eV) | 3.98    | 3.61    | 3.31    | 3.79    |
| Electronegativity (χ) | 3.97    | 3.51    | 4.43    | 4.07    |
| Molecular hardness (η) | 1.99    | 1.81    | 1.65    | 1.89    |
| Transition wavelength λ_gap (nm) | 311.94 | 343.91 | 375.08 | 327.58 |
| Spectral frequency Ψ (nm)^-1 | 0.32    | 0.29    | 0.27    | 0.31    |
| Spectral shift (nm)   | 0.00    | 31.97   | 63.14   | 15.64   |

3.3. Electronic border orbitals

3.3.1. Homo. Taking into account the values obtained in Table 2 for the Homo border orbital, in the case of the mother molecule (molecule I), the energy of said orbital is -5.96 eV; for molecule II, at -5.31 eV, the magnitude of the energy of the parent molecule's Homo orbital increased 10.91%. For molecule III, the energy of the Homo orbital is -6.09 eV, being 2.18% less compared to the Homo of the parent molecule. For molecule VI, of -5.96 eV, the same value of the Homo border orbital was maintained.

3.3.2. Lumo. The Lumo boundary orbital for the parent molecule is -1.98 eV. In the case of molecule II, the energy in the Lumo orbital is -1.70 eV, which compared to the lumo border orbital of the mother molecule, this grew by 14.14%. Para la molécula III el Lumo es de -2.78 eV, el orbital Lumo para la molécula III aumenta, siendo del 40.40% de la magnitud de la energía del orbital Lumo de la molécula I; la energía del orbital de frontera Lumo para la molécula VI es de -2.17 eV, therefore, it decreased 9.60% than the energy of the Lumo boundary orbital of the parent molecule.
3.3.3. **Energy gap.** With the information from the Homo and Lumo boundary orbitals, the energy gap can be found, which is the energy required to supply the system so that the homo boundary electron can jump to the lumo orbital [2,5,11]. It can be seen in Table 2, that for the parent molecular structure (molecule I) the energy gap is 3.98 eV, for derived molecules, the energy gap that decreased the most was that of molecule II with 3.61 eV, decreasing 9.30% of the value of the energy gap of the mother molecule; the energy gap for molecule III is 3.31 eV, compared to the energy gap of the mother molecule, decreased by 16.83% compared to the mother molecule. For molecule IV the energy gap compared to that of the mother structure decreased, being 3.79 eV, equivalent to 4.77% less than the value of the energy gap of the mother molecule. The decrease in the energy gap that the derived molecular structures present compared to the energy gap of the mother molecule, arises as a result of the contribution of the electrons provided by the amino fragment, as presented by Lima (2014) [32] and W Cai (2015) [35], to the molecular electronic system, so new molecular structures will need less energy to make the electronic transition from the homo border orbital to the Lumo border orbital, that is, a bathochromic phenomenon can be predicted in each of the derived molecular structures, which consists of the displacement of the absorption spectrum with lower energy wavelengths.

3.4. **Interpretation of electronegativity**

Electronegativity ($\chi$) is a global molecular descriptor that provides the capacity index of a system to attract electrons [1,16]. This means that the higher the electronegativity index, the greater its ability to attract electrons towards itself. When observing the calculated electronegativity values for the studied structures, in Table 2, it can be seen that the electronegativity of the derived molecules II of 3.51 D and III of 1.61 D, that is, that compared to the mother molecule, these decreased by 11.59% and 58.44%. The decrease in the case of the derived molecule III being greater, which can be understood if the fundamental role played by the contribution of the electron acceptor -NO$_2$ group in the electronic structure is taken into account.

The results show that the electronegativity of molecule IV is 4.07 D, increasing this value found by 2.52% compared to the electronegativity of the mother structure (molecule I), which implies an increase due to the simultaneous influence of the electro-donor group -NH$_2$ and the electro-acceptor group -NO$_2$ of molecular structure VI (see Table 1) which has improved the electronegativity of the molecular structure, thus allowing a greater tendency to capture more electrons than the mother molecule, also the results show that for this molecule, the electronegativity is much higher than that of derived molecules II and III, for being more electronegative.

3.5. **Interpretation of molecular hardness**

Is the global descriptor that measures the resistance that the molecule imposes to the change in its molecular electronic distribution [1,13,23]. When observing the results obtained for molecular hardness ($\eta$) in Table 2, compared to the parent molecular structure (molecule I), it can be seen that the substitution made with the -NH$_2$ electron donor group in molecule II allowed a decrease 9.05%, remaining at 1.81. The -NO$_2$ electron acceptor group in molecule III produced an increase in molecular hardness of 122.61%, this being 4.43. And the Push-pull effect produced by the -NH$_2$ group and -NO$_2$ simultaneously in molecule IV that decreased the molecular hardness by 5.03%, remaining at 1.89.

The decrease in the molecular hardness’s of derived molecules II and IV compared to the molecular hardness of the mother molecule, is the result of the availability of more electrons within the molecular electronic system as a result of the contribution made by the amino group in the molecular structures that possess it, where the degree of delocalization allow the electrons to have greater mobility within the spatial structure of the conjugated pi bonds that overlap to give rise to that entire region within the molecules where the electronic system as a whole of the molecule is held [23], and this causes that the molecular hardness in the derived molecular structures II and IV has decreased compared to the mother molecule. It should be noted that the molecular hardness of molecule II was greater than that of molecule IV, because despite the fact that both possess an electron-acceptor nitro fragment, molecule IV also
possesses the amino fragment of electrons that allows greater mobility of electrons within molecular structure VI, which molecule II does not possess.

3.6. Transition wavelength
In order for the mother molecular structure to make an electronic transition from the Homo orbital to the Lumo orbital, it is necessary to excite an electron with a photon \[ \lambda \] having a wavelength of 311.94 nm, this wavelength in the case of molecule II increased by 10.25%, being 343.91 nm, in the case of molecule III, the wavelength was 375.08 nm, that is to say, which increased compared to the transition wavelength \( \lambda_{\text{Gap}} \) of the photon that the parent molecular structure would need by 20.24%. Finally, for molecule IV, the transition wavelength of the photon that excites the Homo electron is 327.58 nm, showing that it increased by 5.01% compared to the mother molecule, but it is less compared to molecule II and III.

3.7. Spectral shift
The comparison between the difference between the wavelength of the electron of the transition orbital (possibly the Lumo orbital) and the Homo orbital, of the molecular structures under study, is what is commonly known as spectral shift \([3,31]\), that for molecule II it was 31.97 nm, for molecule III it was 63.14 nm and for molecule IV it was 15.64 nm. That is to say, molecule III had a greater spectral shift with reference to the spectrum of the mother molecule, than molecule II and IV. This greater spectral shift occurs due to the influence of the nitro fragment on the mother structure in molecule II, while the influence of the amino group and the push-pull effect in molecules II and IV makes this spectral shift much less.

4. Conclusions
Based on the DFT, using the hybrid functional that combines Becke's three-parameter exchange functional with Lee Yang Parr's correlation functional, the electronic and intrinsic chemical reactivity properties of four organic compounds derived from 1,3-Benzoxazole, with alternating phenyl-oxazole ring molecular structure have been designed and modeled. The study allowed to understand the influence of the induced charge transfer of resonant character, by the substitute fragments electro acceptor -NO\(_2\) and electro donor -NH\(_2\) and its favorable effect to achieve structures with dipolar moments much bigger in comparison with the mother molecule and with smaller energy gap. The individual influence of each substitute and the simultaneous influence on the conjugated pi-link chain of each molecular structure was identified. The results show that the effect of the nitro group is stronger compared to that of the amino group, as could be seen from the changes they induce in the values of the global molecular descriptors used to characterize the electronic properties and intrinsic chemical reactivity of the parent and derived molecules. On the other hand, the simultaneous effect of the two groups mentioned in the molecule 40-Ortoammonium-32-Paranitro-27-Phenyl-30-Oxazole-2-Phenyl-1,3-Benzoxazole gives light to understand these mechanisms to be used in a favorable way for the novel materials development with specific optical properties of absorption and fluorescence, optoelectronics. The results obtained are valuable; since they allow to make a scan within a range of near values and concrete spectral band without having to resort to an enlargement of the molecular chain to ensure a chain of conjugated pi-links suitable for developing applications based on these materials. Finally, it is recommended as a next phase of research, to deepen in the study of the absorption and fluorescence properties of each one of the studied organic derivatives, since it shows a batochronic shift of the absorption bands, conclusion obtained from the value of the wavelength of the electron optical transition from homo to lumo, located in regions close to violet and blue of the optical spectrum.

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