Geometric, electronic and intrinsic chemical reactivity properties of mono- and bi-substituted quinoline derivatives for the ground state in gas phase

O L Neira Bueno¹, L Hincapié H¹ and C García Madrid¹
¹Universidad Popular del Cesar, Valledupar, Colombia.

E-mail: oscarneira@unicesar.edu.co

Abstract. The study of geometric, electronic properties and intrinsic chemical reactivity is presented for the case of Quinoline and three-derived molecules (4-Amino-Quinoline, 3-Phenyl-Quinoline, 4-Amino-3-phenylquinoline). The study was carried for the ground state in gas phase in the context of the functional theory density using B3LYP/631+G (d) model. The purpose of the study is aimed for identifying a compound derived from quinoline, on based to mono- or bi-substitution, using the amino fragment and the phenyl group.

1. Introduction
Organic compounds (OC) with \(\pi\)-conjugated bonds chains occupy an important place in different fields of science [1-12]. Its potential use depends on its optical, optoelectronic and photostability properties among others. All these properties are closely related to the electronic properties and intrinsic chemical reactivity of molecular structures that constitute each material [1-4], OCs play an important role to develop materials of interest as organic electronic materials (semiconductors), organic light emitting diodes [1], field effect transistors [3], solar cells [4], active media [9]. It is known that with an adequate alteration in the molecular structure of organic compounds it is possible to modify its properties [1-12]. On the other hand, the role of the quinoline [12] structure as the basic unit in the family of organic compounds that have ideal properties of absorption and fluorescence has allowed for laser effect in the UV and violet regions [11]. In work [12] found that derivate compounds obtained from the replacement of one of the atoms bonded to a carbon atom into quinoline has good optical properties (See Figure. 1).

2. Theoretical background
The prediction of the reactivity and the selectivity of a chemical process is critical into many organic, inorganic, and biochemical reactions. Thus different theories have been proposed to explain chemical reactivity and/or selectivity. Each theory has proposed a set of global and/or local indexes aiming to describe the chemical processes. Global indexes such as electronegativity (\(\mu\)) [1] and hardness (\(\eta\)) [2]...
have been introduced to characterize the reactivity of a compound. Local indexes, like Fukui’s frontier molecular orbital [6-10] or local softness [6] have been introduced to explain the region and/or stereo selectivity of a reaction. In Density Functional Theory (DFT), the total energy $E$ of a system (the ground-state energy of an atom or a molecule) is expressed as a functional of the electronic density $\rho(r)$, and $v(r)$, in the form [1-6].

$$E[\rho(r)] = F[\rho(r)] + \int v(r)\rho(r)\,dr$$  \hspace{1cm} (1)

Where $v(r)$ is the external potential acting on the interacting system (at minimum, for a molecular system, the electron-nuclei interaction) and $F[\rho]$ is the universal Hohenberg–Kohn functional: $F[\rho] = T[\rho] + V_{\alpha}(\rho)$. $T[\rho]$ represents the electronic kinetic energy functional ($T_{\alpha}$ or $T_{\alpha\beta}$ is the Kohn–Sham kinetic energy). This energy corresponds to the sum of the nuclear interaction energy and the electronic energy of the molecule, which was obtained for the fixed spatial configuration of the nuclei to ensure the minimum energy of the molecular system by approximation of Born-Oppenheimer.

$$E[\rho] = T[\rho] + \int v_{\alpha\beta}(r)\rho(r)\,dr + V_{\alpha} [\rho] + E_{\alpha}[\rho]$$ \hspace{1cm} (2)

DFT provides the theoretical framework for rationalizing molecular reactivity in term of the response of the system toward variation of $N$ and $v(r)$. The response to changes in the number of electrons, when the external potential remains constant, is measured at first order by the chemical potential [3,4],

$$\mu = \left. \frac{\partial E}{\partial N} \right|_{v(r)}$$ \hspace{1cm} (3)

and at second order by the hardness [3,4],

$$\eta = \left. \frac{\partial^2 E}{\partial N^2} \right|_{v(r)}$$ \hspace{1cm} (4)

Definitions of $\mu$ and $\eta$ were given by Parr and Pearson [6-9]. Using a two-point finite difference approximation for chemical potential and a three-point finite difference approximation for the hardness, it leads to the following working definitions of these quantities:

$$\mu = \frac{1}{2} \left[ E(N+1) - E(N-1) \right]$$ \hspace{1cm} (5)

$$\eta = \frac{1}{2} \left[ E(N+1) + E(N-1) - 2E(N) \right]$$ \hspace{1cm} (6)

Where $E(N-1) = IP$ and $E(N+1) = EA$ are the first vertical ionization potential and electron affinity of the neutral molecule, respectively, while $E(N)$ is the energy of the neutral state system. Using the Koopmans’ theorem, ($IP = -\varepsilon_H$ and $EA = \varepsilon_L$) allows one to write $\mu$ and $\eta$ in terms of the energy of frontier HOMO ($\varepsilon_H$) and LUMO ($\varepsilon_L$) molecular orbitals, is obtained finally:
\[ \mu = \frac{1}{2}(\epsilon_1 + \epsilon_2) \cdot \eta = \frac{1}{2}(\epsilon_1 - \epsilon_2) \]  

\( \text{(7)} \)

3. Methodology and computational design
All the calculations obtained have been carried out with the package of programs Gaussian 09 [13], within the framework of density functional theory (DFT), using the three parameter Becke parametrization [6] for the Lee et al [7] exchange-correlation (B3LYP) and 6-31+G(d) basis set.

4. Analysis of obtained results and discussion
The comparison is made for each descriptor of each molecule derived with the value of the parent molecule descriptor. The influence of the substituent in the values of similar chemical bonds between identical atoms within each molecular structure atoms are presented in Table 1 and Table 2 and the values of energy, dipolar moment, reactivity descriptors in Table 3.

| Atoms | Q    | 4AQ  | 3FQ  | 4A3FQ |
|-------|------|------|------|-------|
| C1-C2 | 1.378| 1.379| 1.379| 1.381 |
| C2-C3 | 1.421| 1.422| 1.422| 1.421 |
| C3-C4 | 1.433| 1.435| 1.432| 1.430 |
| C4-C5 | 1.421| 1.421| 1.420| 1.421 |
| C5-C6 | 1.379| 1.378| 1.379| 1.379 |
| C6-C1 | 1.419| 1.419| 1.419| 1.415 |
| C1-H2 | 1.087| 1.087| 1.087| 1.087 |
| C2-H3 | 1.088| 1.085| 1.088| 1.087 |
| C3-C7 | 1.420| 1.427| 1.417| 1.437 |
| C4-N1 | 1.367| 1.366| 1.367| 1.367 |
| C5-H4 | 1.086| 1.086| 1.086| 1.086 |
| C6-H5 | 1.087| 1.087| 1.087| 1.087 |
| C7-C9 | 1.376| 1.381| 1.383| 1.399 |
| C8-C9 | 1.420| 1.417| 1.430| 1.420 |
| C8-N1 | 1.318| 1.318| 1.316| 1.317 |
| C8-H6 | 1.090| 1.090| 1.089| 1.090 |

Table 1. length values of similar chemical bonds between identical atoms within each molecular structure.

| Atoms | Q      | Media | Mediane | Rango | Varianza | D. Estandar | Coef. Var |
|-------|--------|-------|---------|-------|----------|-------------|-----------|
| C1-C2 | 1.378  | 1.379 | 1.379   | 0.002 | 0.0000013| 0.0012      | 0.00084   |
| C2-C3 | 1.421  | 1.422 | 1.422   | 0.001 | 0.0000003| 0.0006      | 0.00041   |
| C3-C4 | 1.433  | 1.433 | 1.432   | 0.005 | 0.0000063| 0.0025      | 0.00176   |
| C4-C5 | 1.421  | 1.421 | 1.421   | 0.001 | 0.0000003| 0.0006      | 0.00041   |
| C5-C6 | 1.379  | 1.379 | 1.379   | 0.001 | 0.0000003| 0.0006      | 0.00042   |
| C6-C1 | 1.419  | 1.418 | 1.419   | 0.004 | 0.0000053| 0.0023      | 0.00163   |
| C1-H2 | 1.087  | 1.087 | 1.087   | 0     | 0.0000000| 0.0000      | 0.00000   |
| C2-H3 | 1.088  | 1.087 | 1.087   | 0.003 | 0.0000023| 0.0015      | 0.00141   |
| C3-C7 | 1.420  | 1.425 | 1.427   | 0.02  | 0.0001000| 0.0100      | 0.00701   |
| C4-N1 | 1.367  | 1.367 | 1.367   | 0.001 | 0.0000003| 0.0006      | 0.00042   |
| C5-H4 | 1.086  | 1.086 | 1.086   | 0     | 0.0000000| 0.0000      | 0.00000   |
| C6-H5 | 1.087  | 1.087 | 1.087   | 0     | 0.0000000| 0.0000      | 0.00000   |
| C7-C9 | 1.376  | 1.385 | 1.383   | 0.018 | 0.0000973| 0.0099      | 0.00713   |
| C8-C9 | 1.420  | 1.422 | 1.420   | 0.013 | 0.0000463| 0.0068      | 0.00479   |
| C8-N1 | 1.318  | 1.317 | 1.317   | 0.002 | 0.0000010| 0.0010      | 0.00076   |
| C8-H6 | 1.090  | 1.090 | 1.090   | 0.001 | 0.0000003| 0.0006      | 0.00053   |

Table 2. Descriptive statistics approach based on dispersion and central tendency for length values of similar chemical bonds.
The most significant changes happen for the angles between identical chemical bonds at the C8-C9-N1, C3-C4-C7 and C1-C6-H5 and C7-C9 bonds. The statistical descriptors of central tendency and dispersion, which are shown in the Tables 1 and 2, it can be inferred that values of different chemical bond lengths are very close to the values of the corresponding bonds in the parent molecule, which shows that despite the changes that causes the fragments substituents in such bonds, from the geometrical point of view, an additional element emerges to affirm that new derivative structures belong to a family of chemical compounds, appearance which is ratified by the range values (10^{-2} to 10^{-3}), variance (10^{-4} to 10^{-5}), the mean square deviation ((10^{-2} to 10^{-3}).

Table 3. Global molecular descriptors of the Quinoline and its three derived molecules for the ground state in gas phase.

| Parameter            | Q                  | 4AQ         | 3FQ            | 4A3FQ        |
|----------------------|--------------------|-------------|----------------|--------------|
| Energy (eV)          | -10937.508892614   | -12443.637280553 | -17225.098294597 | -18731.511286025 |
| Dipolar moment (D)   | 2.1864             | 2.6419      | 2.2203         | 3.6206       |
| HOMO (eV)            | -6.574546354       | -6.428149022 | -6.345154252   | -5.882560452 |
| LUMO (eV)            | -1.750509362       | -1.684657774 | -1.835136816   | -1.50695218  |
| Gap (eV)             | 4.824036992        | 4.743491248 | 4.510017436    | 4.375865234  |
| Chemical potential (eV) | -4.162527858    | -4.056403398 | -4.090145534   | -3.694627835 |
| Hardness             | 2.412018496        | 2.371745624 | 2.255008718    | 2.187932617  |
| Electronegative      | 4.162527858        | 4.056403398 | 4.090145534    | 3.694627835  |

For total energy value, the effect of substituents caused in 4-Amino-Quinoline a decrease of 13.7%, in 3-phenyl-Quinoline of 57.4%, in 4-amino.3-phenyl-Quinoline of 71.2%. i.e. from the energy point of view, they would be more stable. The effects of the respective substituents caused in the dipole moments are in 4-Amino-Quinoline a decrease of 20.8%, in 3-phenyl-Quinoline of 1.5%, in 4-amino.3-phenyl-Quinoline of 65.6%. i.e. from the dipolar moment point of view, It is suggesting that new structures should provide better absorption and fluorescence properties in relation to the quinolone. The values obtained for HOMO energies, allow us to infer that effects of the respective substituents caused an increase of 2.2% in the value of HOMO in 4-Amino-Quinoline, 3.5% in 3-phenyl-Quinoline and 10.5% in 4-amino-3-phenyl-Quinoline i.e. from this point of view, It is suggesting that new structures can more easily donate an electron under similar conditions in an electrophilic solvent or a photon of lower energy is required to ionize the molecules, i.e. ionization potentials of derive molecules are lower compared to that of the parent molecule. Also new molecules have less ability to nucleophilic attack. The values obtained for LUMO energy, allow us to infer that effects of the respective substituents caused an increase of 3.7% in the value of LUMO in 4AQ, decrease 4.6% in 3FQ and increase 13.9% in 4A3FQ, i.e. from this point of view, it is suggesting that is more easy of an attack by nucleophiles for in 3FQ.

Table No 4. Theoretical prediction of the position of an absorption spectrum band.

| Name   | ∆E (eV) | λ_{H→L} (nm) | ∆Q-X | λ_{H→L} (nm) |
|--------|---------|--------------|------|--------------|
| Q      | 4.824   | 257.0153     |      |              |
| 2AQ    | 4.743   | 261.458      | 4.44267 |
| 3FQ    | 4.510   | 274.90952    | 17.89419 |
| 4A3FQ  | 4.375   | 283.3276     | 26.31235 |
should be located about 257 nm, for 4-AQ at 261.6 nm, for 3-phenyl-Quinoleina at 274.9 and finally for 4A3FQ in 283.32768 nm.

5. Conclusions
It was possible to characterize four organic compounds, which constitute Quinoline derivatives, which by their intrinsic properties, chemical reactivity electronic augur possess better optical properties than the parent compound.

References
[1] D Tomkute-Luksiene, J Keruckas, T Malinauskas, J Simokaitiene, V Getautis 213 Dyes and Pigm 96 278
[2] Fuli Zhang, Lian Duan, Juan Qiao, Guifang Dong, Liduo Wang, Yong Qiu 2012 Organic Electro 13 1277
[3] Hungshin Fua, Yi-Ming Chengb, Pi-Tai Choua and Yun Chib 2011 Materials Today 14 476
[4] Frederik C Krebs 2009 Solar Energy Materials & Solar Cells 93 394
[5] Matthew Wright, Ashraf Uddin 2012 Solar Energy Materials & Solar Cells 107 87
[6] Chengteh Lee, Weitao Yang and Robert G Parr 1988 Phys Rev B 37-2 785
[7] D Becke 1988 Phys Rev A 38-6 3098
[8] Parr R G, Yang W 1989 Density-functional theory of atoms and molecules (New York: Oxford University Press)
[9] A V Kukhta, I N Kukhta, N A Kukhta, O L Neyra and E Meza 2008 Journal of Physics B Atomic Molecular and Optical Physics 41-20 205701
[10] R G Parr and W Yang 1995 Annual Review of Physical Chemistry 46-1 701
[11] W Kohn and L J Sham 1965 Phys Rev A 140-4 1133
[12] Pereira Hugo 2015 Influencia de sustituyentes donantes y aceptores de electrones en las propiedades estructurales, de absorción óptica y fluorencia en el compuesto quinoleina: Un enfoque desde la teoría del funcional de la densidad (DFT) (Colombia: Universidad Popular del Cesar)
[13] M J Frisch, G W Trucks, H B Schlegel, G E Scuseria, M A Robb, J R Cheeseman, G Scalmani, et al 2009 Gaussian 09 revision D.01 (Wallingford: Gaussian Inc)