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

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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/6 31+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 π-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).
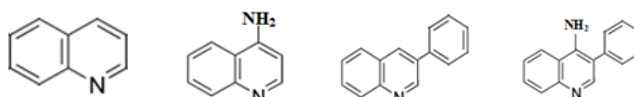

Figure. 1: Molecular structures studied.

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 (μ) [1] and hardness (η) [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].

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

Where $v(r)$, is the external potential acting on the interacting system (at minimum, for a molecular system, the electron-nuclei interaction) and $F\big[\rho\big]$ is the universal Hohenberg–Kohn functional: $F\big[\rho\big] = T\big[\rho\big] + V_{ee}(\rho)$, $T\big[\rho\big]$ represents the electronic kinetic energy functional (T_s or T_{sk} 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.

$$E\big[\rho\big] = T_s\big[\rho\big] + \int v_{ext}(r)\rho(r)d\tau + V_H\big[\rho\big] + E_{xc}\big[\rho\big] \tag{2}$$

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],

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{3}$$

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

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \tag{4}$$

Definitions of μ and η 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:

$$\mu \cong \frac{1}{2}\big[E(N+1) - E(N-1)\big] \tag{5}$$

$$\eta \cong \frac{1}{2}\big[E(N+1) + E(N-1) - 2E(N)\big] \tag{6}$$

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 μ and η in terms of the energy of frontier HOMO (ε_H) and LUMO (ε_L) molecular orbitals, is obtained finally:

$$\mu = \frac{1}{2}\left(\varepsilon_L + \varepsilon_H\right) \; , \; \eta = \frac{1}{2}\left(\varepsilon_L - \varepsilon_H\right) \tag{7}$$

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.

Table 1. length values of similar chemical bonds between identical atoms within each molecular structure.
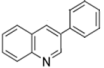
Atoms	Q	4AQ	3FQ	4A3FQ
C1-C2	1.378	1.379	1.379	1.381
C2-C3	1.421	1.422	1.422	1.421
C3-C4	1.433	1.435	1.432	1.430
C4-C5	1.421	1.421	1.420	1.421
C5-C6	1.379	1.378	1.379	1.379
C6-C1	1.419	1.419	1.419	1.415
C1-H2	1.087	1.087	1.087	1.087
C2-H3	1.088	1.085	1.088	1.087
C3-C7	1.420	1.427	1.417	1.437
C4-N1	1.367	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 2. Descriptive statistics approach based on dispersion and central tendency for length values of similar chemical bonds.

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

The most significant changes happen for the angles between identical chemical bonds at the C8-C9-N1, C3-C4-C7 and C1-C6-H5and 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
Molecular descriptors				
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	-1,506695218
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 a electrophilic solvent or a photon of lower energy is required to ionize the molecules, i.e. ionization potentials of derivate 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	ΔE_z (eV)	$\lambda_{H \rightarrow L}$ (nm)	$\Delta^{Q-XQ} \lambda_{H \rightarrow L}$ (nm)
Q		4,824	257,01533
2AQ	4,743	261,458	4,44267
3FQ	4,510	274,90952	17,89419
4A3FQ	4,375	283,32768	26,31235

In Table 4 are presented the values of the wavelengths of the photons that should influence on molecular structures occurring the transition of the electron that is occupying the HOMO to LUMO. The values obtained suggest that the absorption bands of these compounds to the Quinoline, part of it

should be located about 257nm, for 4-AQ at 261.6nm, for 3-phenyl-Quinoleina at 274.9 and finally for 4A3FQ in 283,32768nm.

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 fluorecencia en el compuesto quinoleína: 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)