A Theoretical Investigation on the Corrosion Inhibition of Copper by Quinoxaline Derivatives in Nitric Acid Solution

A. Zarrouk[1,], H. Zarrok[2], R. Salghi[3], B. Hammouti[1], S.S. Al-Deyab[6], R. Touzani[1, 4], M. Bouachrine[5], I. Warad[6], T. B. Hadda[7]*

[1] LCAE-URAC18, Faculté des Sciences, Université Mohammed 1er, Oujda-60000, Morocco.
[2] Laboratoire des Procèdes de Séparation, Faculté des Sciences, Université Ibn Tofail, Kénitra, Morocco.
[3] Equipe de Génie de l'Environnement et Biotechnologie, ENSA, Université Ibn Zohr, BP1136 Agadir, Morocco.
[4] Faculté Pluridisciplinaire de Nador, Université Mohammed Premier, BP 300, Selouane 62700, Nador, Morocco.
[5] UMIM, Faculté Polydisciplinaire de Taza, Université Sidi Mohamed Ben Abdellah, Taza, Morocco.
[6] Petrochemical Research Chair, Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia
[7] Laboratoire de Chimie des Matériaux, Faculté des Sciences, Université Mohammed Premier, Oujda-60000, Morocco.
[*]E-mail: azarrouk@gmail.com

In the present work, a theoretical study of two quinoxaline-type organic compounds, (2*Z*)-2-[(3*E*)-3-(2-oxo-2-phenylethylidene)-3, 4-dihydroquinoxalin-2(1*H*)-ylidene]-1 phenylethanone (Q5) and (*Z*)-2-((*E*)-3-(2-oxo-2-phenylethylidene)-3, 4-dihydroquinoxalin-2(1*H*)-ylidene)-1-phenylethanone (Q6), has been performed using density functional theory (DFT) at the B3LYP/6-31G(d) level in order to elucidate the different inhibition efficiencies and reactive sites of these compounds as corrosion inhibitors. The efficiencies of corrosion inhibitors and the global chemical reactivity relate to some parameters, such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN), the global electrophilicity (ω) and the total energy (TE), were calculated. All calculation has been performed by considering Density Functional Theory (DFT) using the GAUSSIAN03W suite of programs. The calculated results are in agreement with the experimental data on the whole.
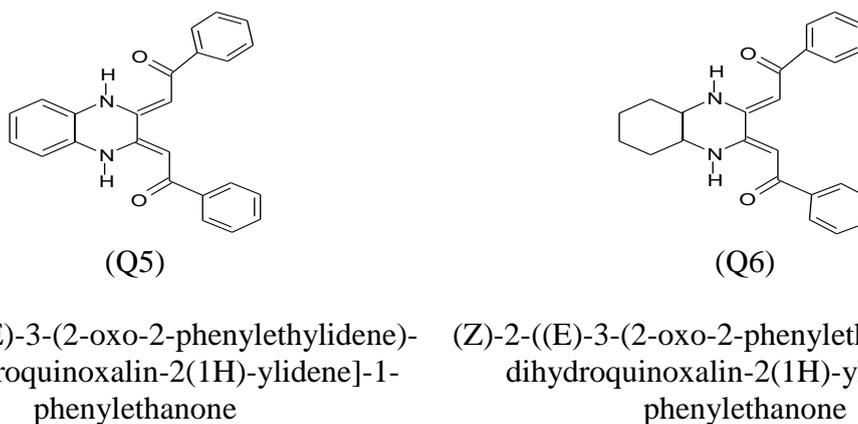
1. INTRODUCTION

Copper and copper alloys are extensively used in various industry applications, both in aqueous and non-aqueous environments. Copper has found considerable use in the electrotechnical industry due to its high electrical conductivity. The conductivity is, next to the conductivity of silver, the highest electrical conductivity at room temperature of all metals [1]. This high value is due to the mall energy difference between the valence and conduction band allowing electrons to flow freely. Copper does not displace hydrogen from acid solutions and it is therefore unattacked in non-oxidising acid environments. Nevertheless, most acidic solutions contain dissolved air that enables some corrosion to take place. Many organic molecules are used to inhibit copper corrosion [2–6]. The primary step in the action of organic corrosion inhibitors in acid solutions is usually adsorption at the metal–solution interface. The adsorption process depends on the electronic characteristic of the molecules (adsorbate), the chemical composition of the solution, nature of the metal surface, temperature of the reaction and on the electrochemical potential at the metal– solution interface [7]. The adsorption requires the existence of attractive forces between the adsorbate and the metal. According to the type of forces, adsorption can be physisorption or chemisorption or a combination of both [8]. Physisorption is due to electrostatic attractive forces between inhibiting organic ions or dipoles and the electrically charged surface of the metal. Chemisorption is due to interaction between unshared electron pairs or π electrons with the metal in order to form a coordinate type of bond. The adsorption occurs from active centers such as P, Se, S, N and O atoms, the double or triple bonds and also aromatic rings. The effect of the molecular structure on the chemical reactivity has been subject of great interest in several disciplines of chemistry. The quantum chemical calculations have been widely used to study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities. This is a useful approach to investigate the mechanisms of reaction in the molecule and its electronic structure level and electronic parameters can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry [9]. The advancement in methodology and implementations has reached a point where predicted properties of reasonable accuracy can be obtained from density functional theory (DFT) calculations [10]. The geometry of the inhibitor in its ground state, as well as the nature of their molecular orbitals, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are involved in the properties of activity of inhibitors. The inhibition property of a compound has been often correlated with energy of HOMO, LUMO and HOMO–LUMO gap. The inhibition efficiency of the two inhibitors was studied previously [11].

The objective of this paper is to investigate the dependence of inhibition efficiency of these compounds on theoretical chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and the total energy (TE). The chemical structures of the compounds studied are given in Fig 1.

(Q5)

(2Z)-2-[(3E)-3-(2-oxo-2-phenylethylidene)-
3,4-dihydroquinoxalin-2(1H)-ylidene]-1-
phenylethanone

(Q6)

(Z)-2-((E)-3-(2-oxo-2-phenylethylidene)-3,4-
dihydroquinoxalin-2(1H)-ylidene)-1-
phenylethanone

Figure 1. The molecular structures of the investigated inhibitors Q5 and Q6.

2. QUANTUM CHEMICAL CALCULATIONS

Complete geometrical optimizations of the investigated molecules are performed using DFT (density functional theory) with the Beck's three parameter exchange functional along with the Lee–Yang–Parr nonlocal correlation functional (B3LYP) [12–14] with 6- 31G* basis set is implemented in Gaussian 03 program package [15]. This approach is shown to yield favorable geometries for a wide variety of systems. This basis set gives good geometry optimizations. The geometry structure was optimized under no constraint. The following quantum chemical parameters were calculated from the obtained optimized structure: The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and the total energy (TE).

3. RESULTS AND DISCUSSION

The inhibition of copper using substituted quinoxalines as corrosion inhibitors were investigated experimentally. Table 1 indicates clearly a decrease in the corrosion rate in the presence of Q5 and Q6. This effect is hugely marked at higher concentration of inhibitors. The inhibitive action is more explicit by E_I% data which increases with inhibitor concentration to reach 82.9% for Q5, 71.9% for Q6. Quantum chemical calculations have been widely used to study reaction mechanisms. They have also proved to be a very powerful tool for studying corrosion inhibition mechanisms [16]. Recently, theoretical prediction of the efficiency of corrosion inhibitors has become very popular in parallel with the progress in computational hardware and the development of efficient algorithms which assisted the routine development of molecular quantum mechanical calculations [17]. All quantum chemical properties were obtained after geometric optimization with respect to the all nuclear

coordinates using Kohn–Sham approach at DFT level. The optimized structure of the studied compound as shown in Fig. 2.

Table 1. Summarized the inhibition efficiency ($E_I\%$) obtained by addition of Q5 and Q6 at different concentrations on the corrosion of copper in 2M HNO_3 solution determined by potentiodynamic polarization [11].

	Conc (M)	E_{corr} (mV/SCE)	$-b_c$ (mV/dec)	I_{corr} ($\mu A/cm^2$)	EI (%)
HNO_3	2	34.0	304	365.1	-
	10^{-3}	-04.2	182	062.2	82.9
Q5	10^{-4}	11.8	185	126.2	65.4
	10^{-5}	14.6	167	291.8	20.1
	10^{-6}	15.9	179	328.5	10.0
	10^{-3}	20.1	190	102.5	71.9
Q6	10^{-4}	20.5	190	153.8	57.9
	10^{-5}	25.9	205	290.7	20.4
	10^{-6}	264	193	315.1	13.7

Q5   Q6
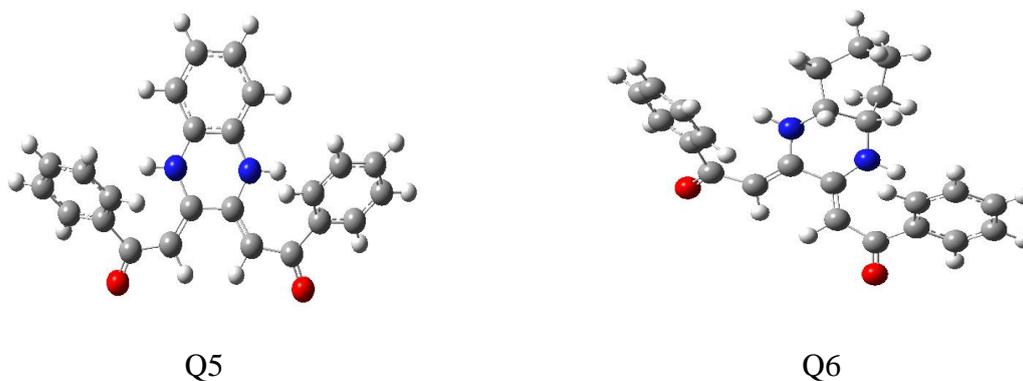
Figure 2. Optimized structure of studied molecules obtained by B3LYP/6-31G* level.

The frontier orbital (highest occupied molecular orbital HOMO and lowest unoccupied molecular orbital LUMO) of a chemical species are very important in defining its reactivity. Fukui first recognized this. A good correlation has been found between the speeds of corrosion and E_{HOMO} that is often associated with the electrondonating ability of the molecule. Survey of literature shows that the adsorption of the inhibitor on the metal surface can occur on the basis of donor–acceptor interactions between the π-electrons of the heterocyclic compound and the vacant d-orbital of the metal surface atoms [18], high value of E_{HOMO} of the molecules shows its tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbitals. Increasing values of E_{HOMO} facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through

the adsorbed layer. Similar relations were found between the rates of corrosion and ΔE ($\Delta E = E_{LUMO} - E_{HOMO}$) [19–21]. The energy of the lowest unoccupied molecular orbital indicates the ability of the molecule to accept electrons. The lower the value of E_{LUMO}, the more probable the molecule would accept electrons. Consequently, concerning the value of the energy gap ΔE, larger values of the energy difference will provide low reactivity to a chemical species. Lower values of the ΔE will render good inhibition efficiency, because the energy required to remove an electron from the lowest occupied orbital will be low [22]. Another method to correlate inhibition efficiency with parameters of molecular structure is to calculate the fraction of electrons transferred from inhibitor to metal surface. According to Koopman's theorem [23], E_{HOMO} and E_{LUMO} of the inhibitor molecule are related to the ionization potential (I) and the electron affinity (A), respectively. The ionization potential and the electron affinity are defined as I = - E_{HOMO} and A = - E_{LUMO}, respectively. Then absolute electronegativity (χ) and global hardness (η) of the inhibitor molecule are approximated as follows [22]:

$$\chi = \frac{I + A}{2} \qquad (1)$$

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

The global electrophilicity index was introduced by Parr [24] and is given by:

$$\omega = \frac{\mu^2}{2\eta} \qquad (3)$$

Thus the fraction of electrons transferred from the inhibitor to metallic surface, ΔN, is given by [25]:

$$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2(\eta_{Cu} + \eta_{inh})} \qquad (4)$$

In order to calculate the fraction of electrons transferred, a theoretical value for the electronegativity of bulk copper was used χ_{Cu}= 4.48 eV/mol [23], and a global hardness of , $\eta_{Cu} = 0$ eV/mol by assuming that for a metallic bulk $I = A$ [26] because they are softer than the neutral metallic atoms.

Quantum chemical parameters obtained from the calculations which are responsible for the inhibition efficiency of inhibitors, such as the highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), HOMO–LUMO energy gap (ΔE_{H-L}), dipole moment (μ) and total energy (TE), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), The global electrophilicity (ω), the fraction of electrons transferred from the inhibitor to iron surface (ΔN) and the total energy (TE) , are collected in Table 2.

Table 2. Calculated quantum chemical parameters of the studied compounds.

Quantum parameters	Q5	Q6
E_{HOMO} (eV)	-5.4378	-5.540
E_{LUMO} (eV)	-2.17812	-1.964
ΔE gap (eV)	3.259	3.576
μ (debye)	8.1609	9.6768
EI (%)	82.9	71.9
$I = -E_{HOMO}$ (eV)	5.4378	5.540
$A = -E_{LUMO}$ (eV)	2.17812	1.964
$\chi = \dfrac{I + A}{2}$ (eV)	3.80796	3.752
$\eta = \dfrac{I - A}{2}$ (eV)	1.62984	1.788
$\sigma = \dfrac{1}{\eta}$	0.61356	0.55928
$\omega = \dfrac{\mu^2}{2\eta}$	20.43154	26.18581
$\Delta N = \dfrac{\chi_{Cu} - \chi_{inh}}{2(\eta_{Cu} + \eta_{inh})}$	0.54766	0.65083
TE (eV)	-1185.3283101	-1188.9302589

In Fig. 3, we have presented the frontier molecule orbital density distributions of the studied compounds: HOMO (right); LUMO (left). Analysis of Fig. 3 shows that the distribution of two energies HOMO and LUMO, we can see that the electron density of the HOMO location in the Quinoxaline molecules is mostly distributed near the nitrogen (NH) and oxygen (= O) atoms and quinoxaline ring indicating that these are the favorite sites for adsorption, while the density LUMO was distributed almost of the entire molecules.

HOMO   **LUMO**

Q5
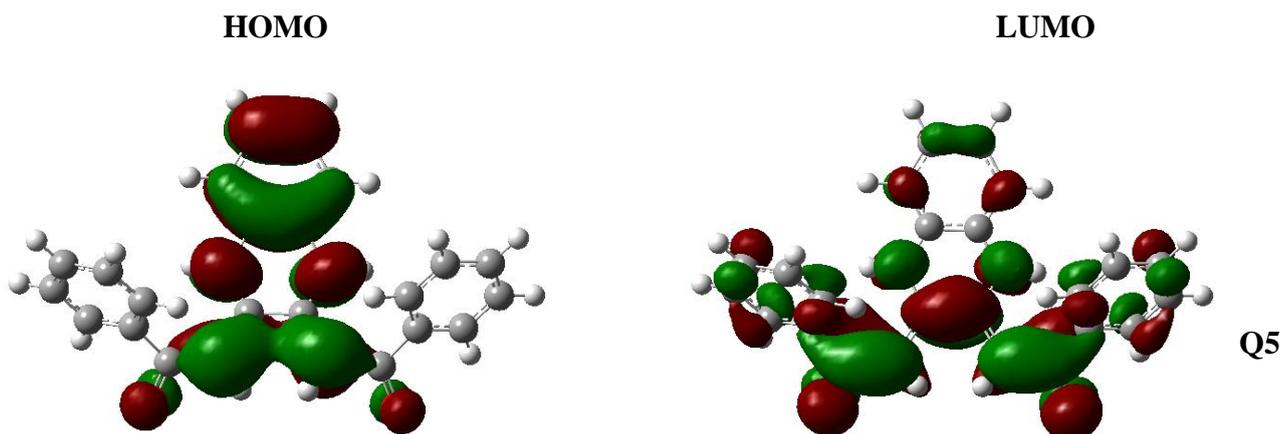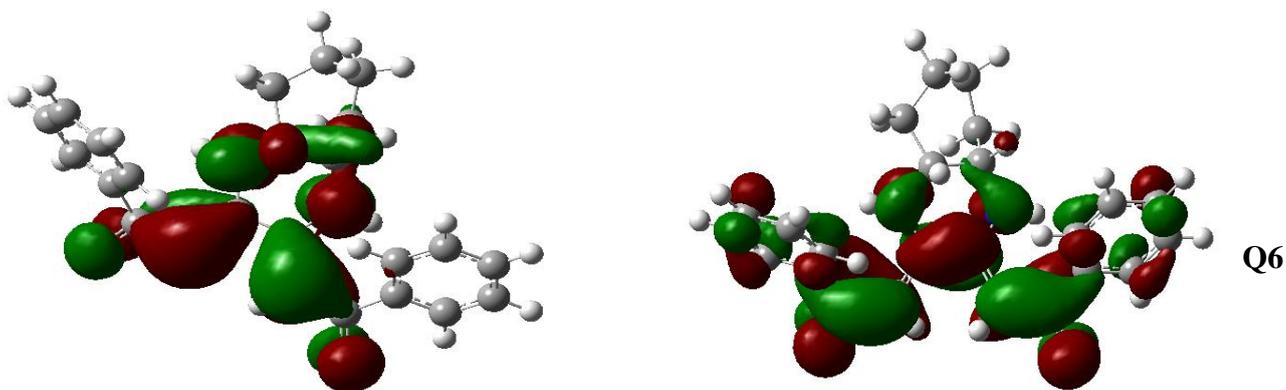
Figure 3. Schematic representation of HOMO and LUMO molecular orbital of studied molecules.

According to the frontier molecular orbital theory (FMO) of chemical reactivity, transition of electron is due to interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species [27]. E_{HOMO} is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [28]. The inhibitor does not only donate electron to the unoccupied d orbital of the metal ion but can also accept electron from the d-orbital of the metal leading to the formation of a feed back bond. The highest value of E_{HOMO} -5.4378 (eV) of **Q5** indicates the better inhibition efficiency.

It has also been found that an inhibitor does not only donate an electron to the unoccupied d orbital of the metal ion but can also accept electrons from the d orbital of the metal leading to the formation of a feedback bond. Therefore, the tendency for the formation of a feedback bond would depend on the value of E_{LUMO}. The lower the E_{LUMO}, the easier is the acceptance of electrons from the d orbital of the metal [21]. Based on the values of E_{LUMO}, the order obtained for the decrease in inhibition efficiency (Q5 > Q6) was also similar to the one obtained from experimental results.

The separation energy, $\Delta E = E_{LUMO} - E_{HOMO}$ is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on metallic surface. As ΔE decreases, the reactivity of the molecule increases leading to increase the inhibition efficiency of the molecule. The results obtained from quantum chemical calculation are listed in Table 2. The calculations indicate that Q5 has the lowest value which means the highest reactivity among the other inhibitor and accordingly the highest inhibition efficiency which agrees well with the experimental observations. The order of reactivity in this case will be:

Q5 > Q6.

Absolute hardness and softness are important properties to measure the molecular stability and reactivity. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [29]. In our present study **Q5** with low hardness value 1.62984 (eV) compared with

other compound have a low energy gap. Normally, the inhibitor with the least value of global hardness (hence the highest value of global softness) is expected to have the highest inhibition efficiency [30]. For the simplest transfer of electron, adsorption could occur at the part of the molecule where softness (σ), which is a local property, has a highest value [19]. Q5 with the softness value of 0.61356 has the highest inhibition efficiency.

The most widely used quantity to describe the polarity is the dipole moment of the molecule [31]. Dipole moment is the measure of polarity of a polar covalent bond. It is defined as the product of charge on the atoms and the distance between the two bonded atoms. The total dipole moment, however, reflects only the global polarity of a molecule. For a complete molecule the total molecular dipole moment may be approximated as the vector sum of individual bond dipole moments. The dipole moment (μ in Debye) is another important electronic parameter that results from non uniform distribution of charges on the various atoms in the molecule. The high value of dipole moment probably increases the adsorption between chemical compound and metal surface [32]. The energy of the deformability increases with the increase in μ, making the molecule easier to adsorb at the Cu surface. The volume of the inhibitor molecules also increases with the increase of μ. This increases the contact area between the molecule and surface of copper and increasing the corrosion inhibition ability of inhibitors. In our study, there is no direct relationship between the $E_I(\%)$ and the dipole moment.

In literature it has been reported that the values of ΔN show inhibition effect resulted from electrons donation [23, 33]. According to Lukovits's study [33], if the value of ΔN < 3.6, the inhibition efficiency increased with increasing electron donating ability of inhibitor at the metal surface. Also it was observed [34] that inhibition efficiency increased with increase in the values of ΔN. However, our study reveals that there is no regular trend in the inhibition efficiency by increasing values of ΔN.
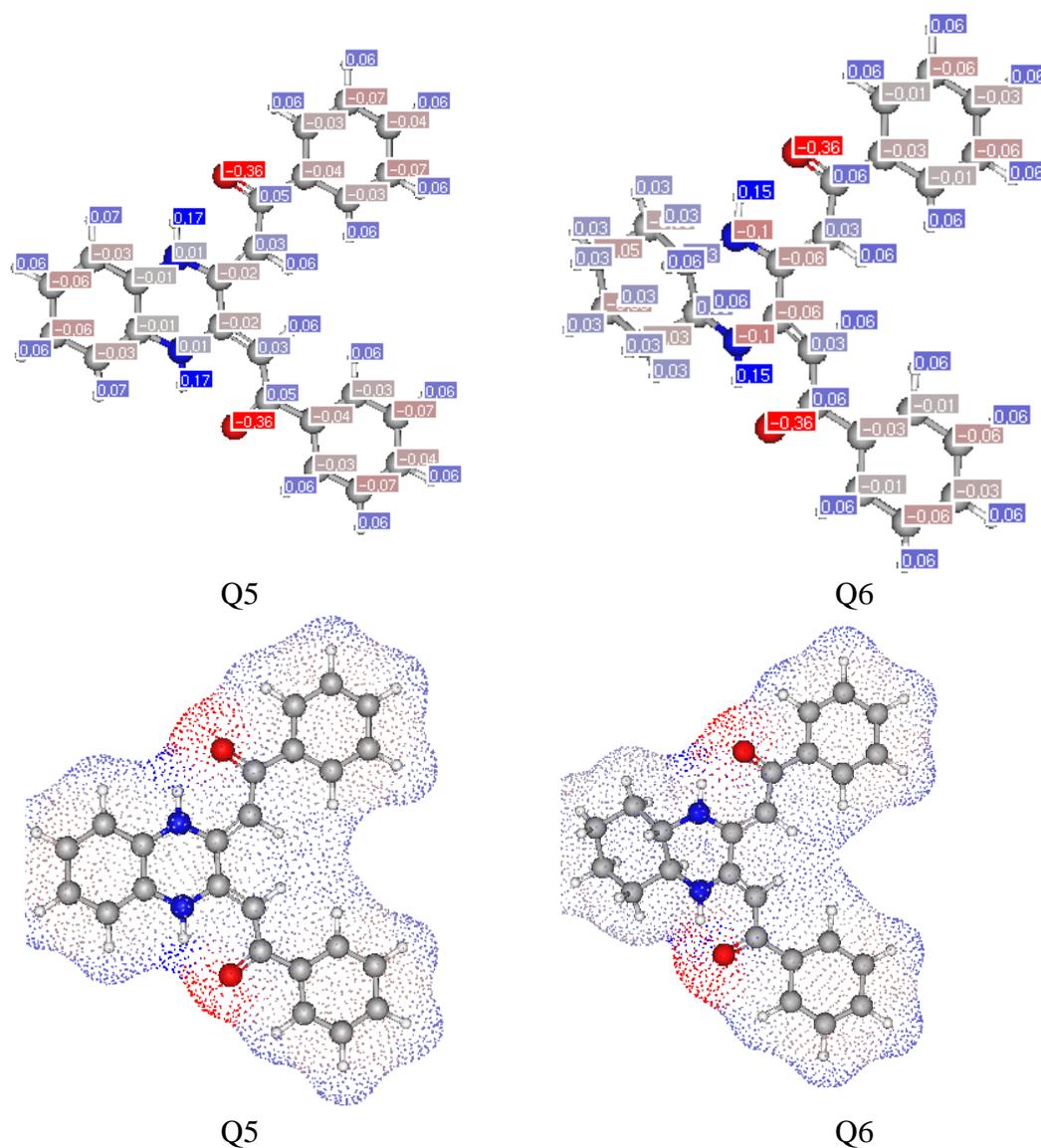
The total energy calculated by quantum chemical methods is also a beneficial parameter. The total energy of a system is composed of the internal, potential, and kinetic energy. Hohenberg and Kohn [35] proved that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy. In our study the total energy of the best inhibitor Q5 is equal to -1185.3283101 eV, this value is lower than that of the compound Q6.
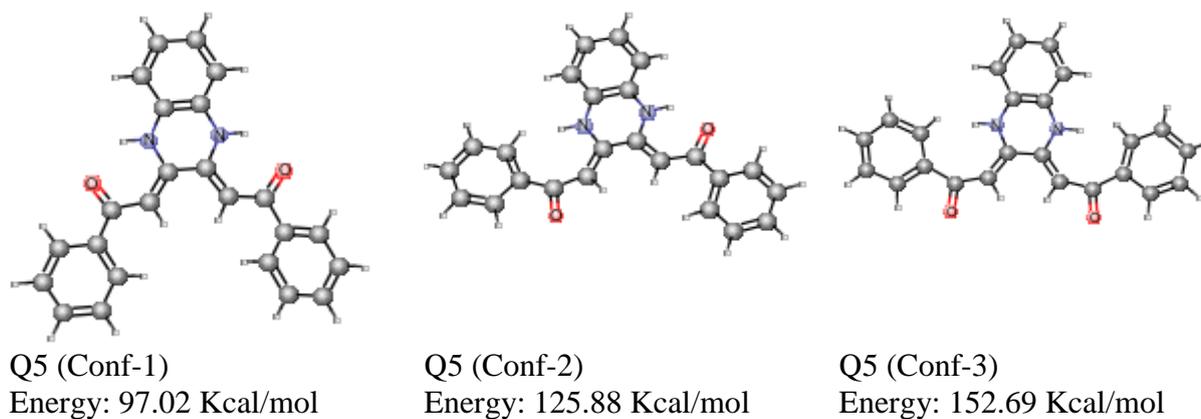
Analysis of charge repartition of compounds Q5 and Q6

The comparison of the reparation atomic charge (Fig. 4) of Q5 and Q6 shows no evident and apparent difference but the look for lowest energy conformer of Q5 and Q6 lead us to conformers1 which have respective energy of 97.02 and 92.38 Kcal/mol (Fig. 5).
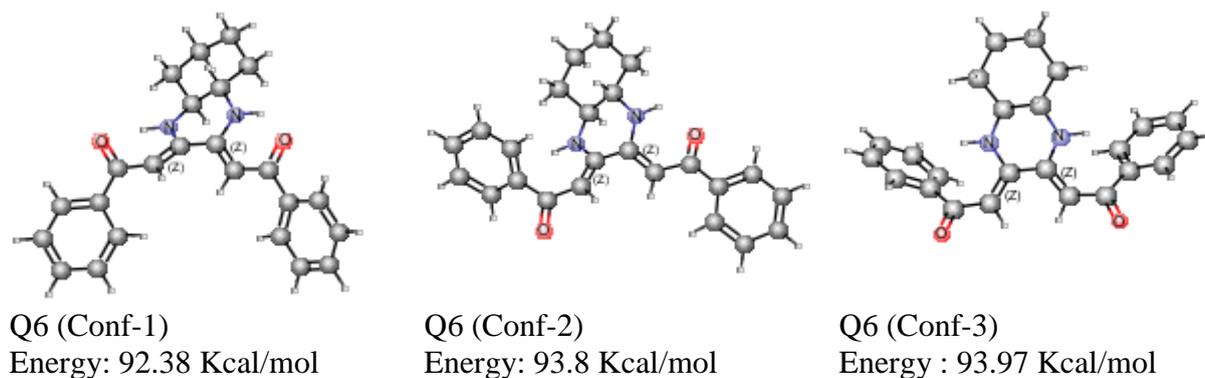
Crystalline structure analysis of compound Q5

The crystalline structure of Q5 (Fig. 6) is fully in agreement with the structures proposed for conformer 1 with lowest energy. The molecule is quasi-planar [36] with a C symmetry axis: the external phenyl rings are twisted by 25 °.

Figure 4. Charge repartition of quinoxalines Q5 and Q6.

Q5 (Conf-1)
Energy: 97.02 Kcal/mol

Q5 (Conf-2)
Energy: 125.88 Kcal/mol

Q5 (Conf-3)
Energy: 152.69 Kcal/mol

Q6 (Conf-1)
Energy: 92.38 Kcal/mol

Q6 (Conf-2)
Energy: 93.8 Kcal/mol

Q6 (Conf-3)
Energy : 93.97 Kcal/mol

Figure 5. Lowest and highest energy conformers of quinoxalines Q5 and Q6.

The nitrogen atom N(1) is trivalent with an N(1)-H(1) bond length of about 0.88 A, confirming the position of the acidic proton. In addition, N(1), C(2), C(8a) and H(1) are perfectly coplanar, resulting from the sp2 hybridization of the nitrogen atom due to the conjugation with the delocalized pi-system. The C(9)-C(10) and C(2)-C(3) distances [1.431(2) and 1.482(3) A, respectively] lie in between single and double bond lengths, confirming the high electronic delocalization. The H(1) --- O(1) distance of about 1.8 A. and the N(1), H(1), O(1) angle of ca. 15°, suggests an intra-molecular N(1)-H(1) --- O(1) hydrogen bond in accordance with the strong NMR deshielding of H(1) [15.0 ppm].[37]
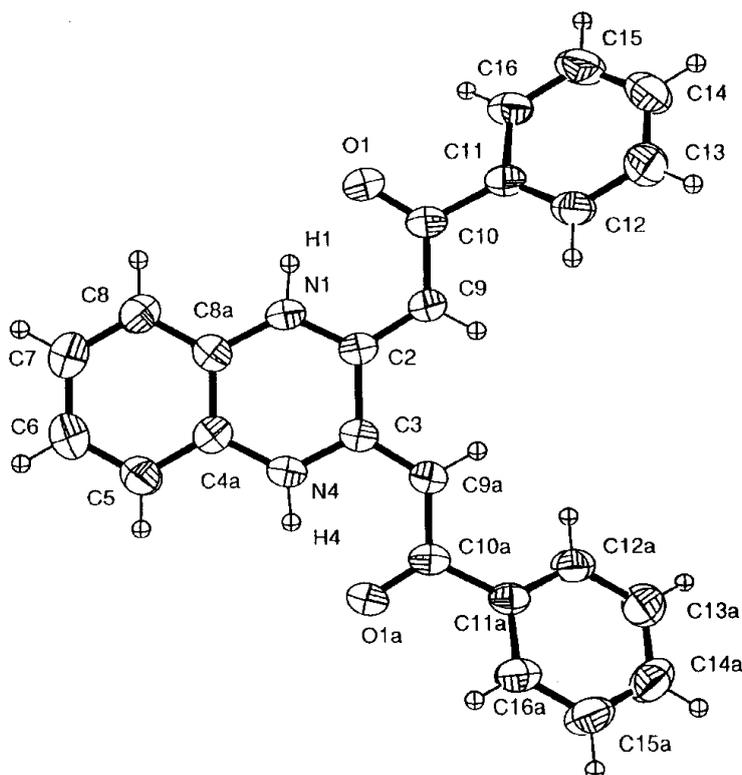
Figure 6. ORTEP drawing of compound **Q5**.

4. CONCLUSION

The correlation between the quantum chemical parameters and inhibition efficiency of some quinoxaline compounds was investigated using DFT/B3LYP calculations. The inhibition efficiency of the inhibitor are closely related to the quantum chemical parameters, the highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), HOMO–LUMO energy gap (ΔE_{H-L}), the hardness (σ), the softness (η) and the fraction of electrons transferred (ΔN) for the neutral inhibitors and no significant relationship was found with parameters, dipole moment (μ) and the total energy (TE).

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