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Research Article

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A theoretical investigation on the corrosion inhibition of mild steel by piperidine derivatives in hydrochloric acid solution

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ABSTRACT

Two piperidin derivatives namely 5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)penta-2,4-dien-1-one (piperine: P1) and 5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)pent-2-en-1-one (piperanine: P2) were investigated as corrosion inhibitors for mild steel using density functional theory (DFT) at B3LYP/6-31G(d) level. Quantum chemical parameters most relevant to their potential action as corrosion inhibitors such as E_{HOMO} *(highest occupied molecular orbital energy),* E_{LUMO} *(lowest unoccupied molecular orbital energy), energy gap (*ΔE*), dipole moment (*μ*), electron affinity (A), ionization potential (I), absolute electronegativity (*χ*), global hardness (*η*), softness (S), fraction of electrons transferred (*ΔN*), electrophilicity index (*ω*) and back-donation (*$\Delta E_{back\text{-}donation}$*), have been calculated and discussed. The theoretical results were found to be consistent with the experimental data reported.*

Keywords: Corrosion**;** Acid solutions; Green inhibitor; Adsorption, DFT

INTRODUCTION

The degradation of materials and their properties due to corrosion of mild steel is a detrimental process that produces huge economic losses resulting in many investigations and researches [1, 2]. One of the most common, effective and economic method to protect metals against corrosion is use of organic compounds (containing heteroatoms having higher basicity and electron density like nitrogen, oxygen and sulphur) as corrosion inhibitors [3, 4]. Most efficient inhibitors are organic compounds containing electronegative functional groups and / or π-electrons in triple or conjugated double bonds. The physicochemical properties of the inhibitor, such as the functional group, molecular electronic structure, steric factors, aromaticity and electron density at the donor atoms, orbital character and the molecular size are important features that determine adsorption on the metal surface [5, 6]. The molecular adsorption on the metallic surface is mainly determined by the planarity and the lone electron pairs in the hetero atoms [7]. The inhibition efficiency is closely related to the molecular structure of the inhibitor (number of active adsorption centers in the molecule, the nature of metal, and the aggressive solution), its adsorption abilities [8, 9] and its electronic structure [10]. Excellent corrosion inhibitors represented by organic compounds behaving, at the same time, on the one hand as electron donors to unoccupied d orbital of metal surface to form coordinate covalent bonds, and in the other hand as acceptor of free electrons from the metal surface by using their anti bonding orbitals to form feedback bonds [11]. The nucleophile centres of inhibitor molecules are represented by lone pairs on hetero atoms or π electrons that are readily available for sharing to form a bond and greatly facilitate the adsorption process over the metal surface, whose atoms act as electrophiles [12]. Hence, the effective inhibitor can adsorb on the metal surface, block the active sites on the surface and thereby reduce the corrosion rate.

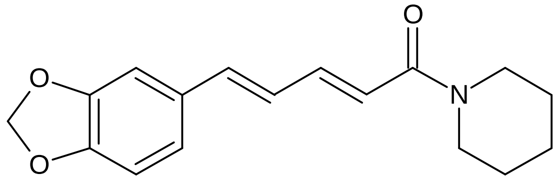
The corrosion of mild steel and iron has formed a tremendous theoretical and practical area of chemical research. Quantum chemical calculations have been widely used to study the reactivity of organic compounds [13, 14] and have been proved to be a powerful tool for studying corrosion inhibition mechanism [15-17]. Khaled [18], realized a correlation between experimental efficiencies of inhibitors and the results of quantum chemical calculations, and constructed a composite index of some of the key quantum chemical parameters in order to characterize the inhibition performance of the tested molecules.

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 [19]. 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.

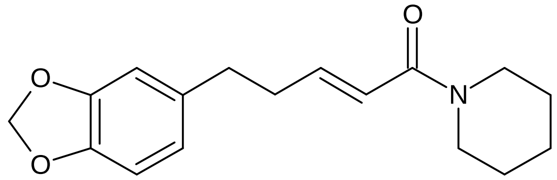
The environmental toxicity of organic corrosion inhibitors paved the way for the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. In the present study we will focus on two of these green corrosion inhibitors that have been characterized recently in our laboratory [20, 21].

THEORY AND COMPUTATIONAL DETAILS

The inhibition potentials of two piperidin derivatives: 5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)penta-2,4-dien-1-one (piperine: P1) and 5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)pent-2-en-1-one (piperanine: P2), Figure 1, have been elucidated using quantum chemical calculations based on density functional theory (DFT). Hence, we have investigated the relationship between the molecular, the electronic structure and the inhibition efficiency of the two studied molecules.



5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)penta-2,4-dien-1-one (piperine: P1)



5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)pent-2-en-1-one (piperanine: P2)

Figure 1: Names, molecular structures and the abbreviations of the inhibitors investigated

The frontier orbital HOMO and LUMO of a chemical species are very important in defining its reactivity. 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 [22], 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 ($\Delta E = E_{LUMO} - E_{HOMO}$) [23-25]. 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 [26]. 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 [27], 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 [26]:

$$\chi = \frac{I + A}{2}$$

$$\eta = \frac{I - A}{2}$$

As hardness (η), softness (S) is a global chemical descriptor measuring the molecular stability and reactivity and is given by:

$$S = \frac{1}{\eta}$$

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 [27].

The global electrophilicity index was introduced by Parr [28] as a measure of energy lowering due to maximal electron flow between donor and acceptor and is given by:

$$\omega = \frac{\mu^2}{2\eta}$$

According to the definition, this index measures the propensity of chemical species to accept electrons. A good, more reactive, nucleophile is characterized by lower value of μ, ω; and conversely a good electrophile is characterized by a high value of μ, ω. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment. Thus the fraction of electrons transferred from the inhibitor to metallic surface, ΔN, is given by [29]:

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

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule, respectively. η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule, respectively. In order to calculate the fraction of electrons transferred, a theoretical value of χ_{Fe}=7.0 eV [29] and $\eta_{Fe} = 0$ by assuming that for a metallic bulk I = A [30] because they are softer than the neutral metallic atoms.

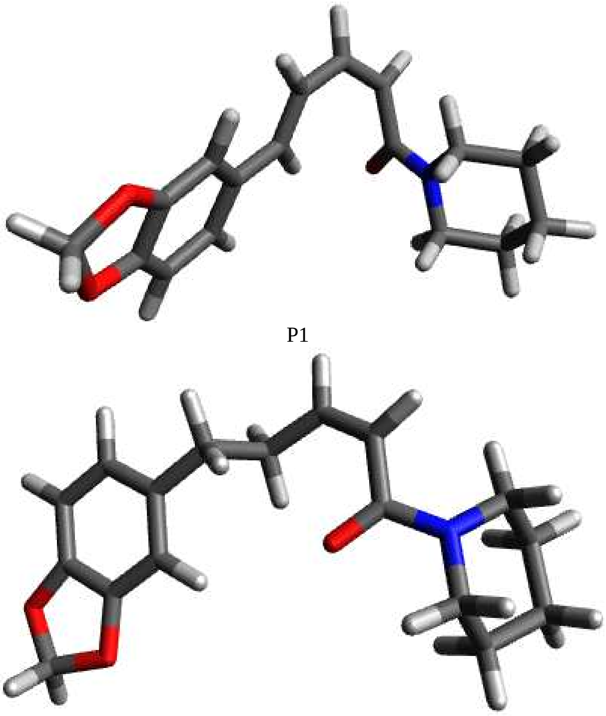
According to the simple charge transfer model for donation and back-donation of charges [31] an electronic back-donation process might be occurring governing the interaction between the inhibitor molecule and the metal surface. The concept establishes that if both processes occur, namely charge transfer to the molecule and back-donation from the molecule, the energy change is directly proportional to the hardness of the molecule, as indicated in the following expression.

$$\Delta E_{\text{back donation}} = -\frac{\eta}{4}$$

The $\Delta E_{\text{back donation}}$ implies that when $\eta > 0$ and $\Delta E_{\text{back donation}} < 0$ the charge transfer to a molecule, followed by a backdonation from the molecule, is energeically favored. In this context, hence, it is possible to compare the stabilization among inhibiting molecules, since there will be an interaction with the same metal, then, it is expected that it will decrease as the hardness increases.

RESULTS AND DISCUSSION

Full geometry optimizations (Figure 2) with no constraints of the two molecules under study (P1 and P2) were performed using DFT based on Beck's three parameter exchange functional and Lee–Yang–Parr nonlocal correlation functional (B3LYP) [32-34] and the 6-31G* orbital basis sets for all atoms as implemented in Gaussian 09 program [35]. This approach has been proved to be a very powerful tool for studying corrosion inhibition mechanism [15-17].



P1

P2

Figure 2: Optimized structures of the compounds P1 and P2 as calculated at the B3LYP/6-31G* level

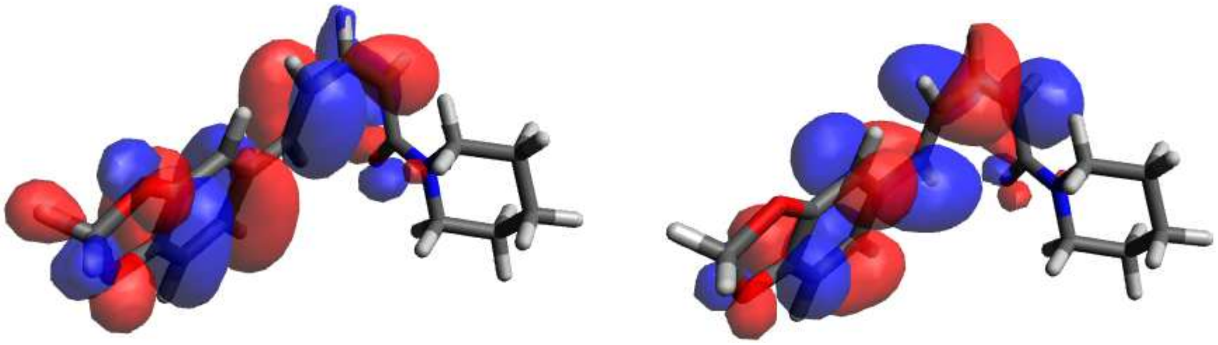
The quantum chemical parameters of P1 and P2 such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), ionization potential (I), electron affinity (A), absolute electronegativity (χ), global hardness (η), global electrophilicity index (ω), softness (S), fraction of electrons transferred (ΔN) and back donation energy ($\Delta E_{back\ donation}$) were calculated and gathered in Table 1.

Table 1: Calculated quantum chemical parameters of the studied molecules

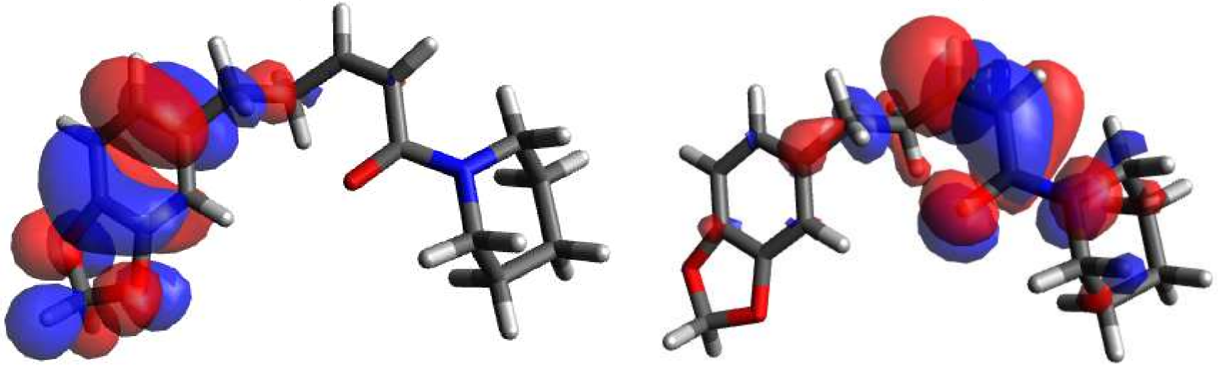
	P1	P2
E_{HOMO} (eV)	-5.270031089	-5.267309949
E_{LUMO} (eV)	-1.268323174	-0.670760915
$\Delta E = E_{LUMO} - E_{HOMO}$ (eV)	4.001707915	4.596549034
$I = -E_{HOMO}$ (eV)	5.270031089	5.267309949
$A = -E_{LUMO}$ (eV)	1.268323174	0.670760915
χ (eV)	3.269177132	2.969035432
η (eV)	2.000853958	2.298274517
μ (debye)	3.6976	3.4766
ω	3.421039289	2.63467221
S	0.499786602	0.435109032
ΔN	0.932307642	0.876954545
IE (%)	98.9 [49]	97.5 [50]

The inhibition effect of a given compound is usually ascribed to adsorption of the molecule on metal surface. There can be physical adsorption (physisorption) and chemical adsorption (chemisorption) depending on the adsorption strength. When chemisorption takes place, one of the reacting species acts as an electron pair donor and the other one act as an electron pair acceptor. The energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbital. Increasing values of E_{HOMO} facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on mild steel and therefore better inhibition efficiency. In this context, survey of Table 1 shows that, the E_{HOMO} of inhibitors P1 and P2 are almost the same: -5.270031089 (eV) and -5.267309949 (eV), respectively. This result is in good agreement with the experiment where the inhibition efficiency (IE) for these compounds is comparable: (98.9 and 97.5 for inhibitors P1 and P2, respectively).

The ground state geometry of the inhibitor as well as the nature of its frontier molecular orbitals, namely, the HOMO and LUMO are involved in the activity properties of the inhibitors. Noteworthy, the shape of the HOMO and LUMO is structural dependant as shown in Figure 3. The electron density of the HOMO location in the inhibitors under study is mostly distributed on the atoms having a delocalized character indicating that these are the favorite adsorption sites. The HOMO and LUMO are strongly localized for the molecules P1 and P2 (due to non planarity of these molecules). Noteworthy, a comparison of the shape of the frontier molecular orbitals HOMO and LUMO shows that the delocalisation in P1 inhibitor is enhanced by the presence of a double bond on the middle of the molecule (simple bond for P2 inhibitor).



HOMO (P1) LUMO (P1)



HOMO (P2) LUMO (P2)

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 [36]. 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 feedback bond. The energy of the lowest unoccupied molecular orbital, $E_{LUMO,}$ indicates the ability of the molecule to accept electrons. The binding ability of the inhibitor to the metal surface increases with increasing of the HOMO and decreasing of the LUMO energy values. Therefore, the lower the value of E_{LUMO} is the more probable the molecule to accept electrons. In our studies the inhibitor P1 having low value of E_{LUMO} -1.268323174 could have better performance as corrosion inhibitor. This is in good agreement with the experiment where P1 inhibitor is more efficient than P2 one.

Energy gap is an important parameter as a function of reactivity of the inhibitor molecule toward the adsorption on the metallic surface. As ΔE decreases, the reactivity of the molecule increases leading to increase in the %IE of the molecule. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low [37]. A molecule with a low energy gap is more polarization and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule [27]. In our study, the trend for the (ΔE) values follows the order P2 > P1, which suggests that P1 (ΔE = 4.00170715 eV) has the highest reactivity in comparison to the other compound P2 and would therefore likely interact strongly with the metal surface. The results as indicated in Table 1 show that inhibitor P1 has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor.

The dipole moment μ (Debye) is another important electronic parameter that results from non uniformed 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 [38]. The energy of the deformability increases with the increase in μ, making the molecule easier to adsorb at the Fe 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 iron and increasing the corrosion inhibition ability of inhibitors. In our study the value 3.6976 (Debye) of P1 enumerates its better inhibition efficiency.

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 [39]. In the present study, the inhibitor P1 with low hardness value 2.000853958 (eV) compared with the other compound P2 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 [12]. For the simplest transfer of electron, adsorption could occur at the part of the molecule where softness (S), which is a local property, has a highest value [40]. P1 with the softness value of 0.499786602 has the highest inhibition efficiency.

The absolute electronegativity is the chemical property that describes the ability of a molecule to attract electrons towards itself in a covalent bond. According to Sanderson's electronegativity equalization principle [41], the molecule P1 with a high electronegativity quickly reaches equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency. The Table 1 shows the order of electronegativity as P1 > P2. Hence an increase in the difference of electronegativity between the metal and inhibitor is observed in the order P1 > P2.

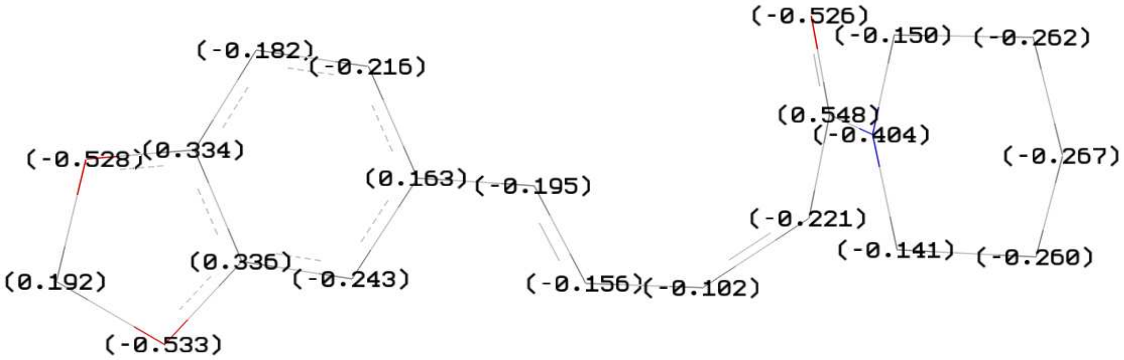
The number of electrons transferred (ΔN) was also calculated and tabulated in Table 1. Values of (ΔN) show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [42]. If $\Delta N < 3.6$, the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface and it increases in the following order: P1 > P2. The results indicate that ΔN values correlates strongly with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is associated with the best inhibitor P1, while the least fraction is associated with the inhibitor that has the least inhibition efficiency P2. The Inhibitor P1 with the ΔN value of 0.9323 has the highest inhibition efficiency.

The global electrophilicity index, ω, shows the ability of the inhibitor molecules to accept electrons. It is a measure of the stabilization in energy after a system accepts additional amount of electron charge ΔN from the environment [28]. In our case, the inhibitor P1 with high electrophilicity index value (3.421039289) than the other compound is the strongest nucleophile and therefore has the highest inhibition efficiency [43].

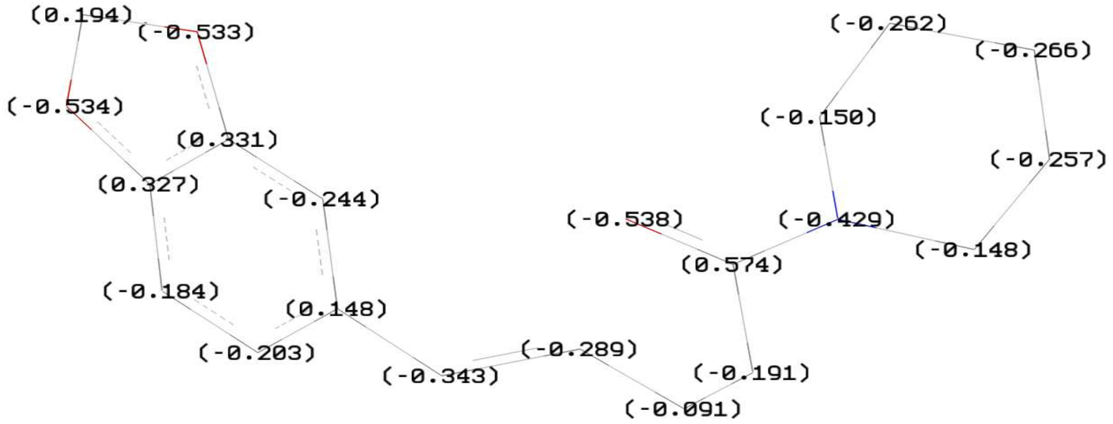
The calculated $\Delta_{\text{Eback donation}}$ values for the inhibitors as listed in Table 1 reveal that the order followed is: P1 > P2, which indicates that back-donation is favored for the P1 molecule which is the best inhibitor.

Figure 4 representing the effective atomic charges from Mulliken poupulations of the inhibitors P1 and P2, shows that oxygen atoms in benzodioxol ring, some carbone atoms of benzodioxol ring, carbone atoms of the two double bonds for P1 (respectively one double bond for P2), nitrogen and carbon atoms of the pyridine ring, and oxygen atom of the carbonyl group carry more negative charges, while the remaining heavy atoms carry more positive charges. This means that the atoms carrying negative charges are the negative charge centers, which can offer electrons to the Fe atoms to form coordinate bond, and the atoms carrying positive charges are the positive charge centers, which can accept electrons from orbital of Fe atoms to form feedback bond. We emphasize also that the most negatively charged atoms are the three oxygen atoms followed by the nitrogen atom.

The optimized structure is in accordance with the fact that excellent corrosion inhibitors cannot only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal. Therefore, it can be inferred that benzodioxol ring, the two double bonds for P1 (respectively only one double bond for P2), pyridine ring, and oxygen atom of the carbonyl group are the possible active adsorption sites.



P1



P2

Figure 4: Effective atomic charges of heavy atoms from Mulliken poupulations of P1 and P2

CONCLUSION

The inhibition efficiency of two piperidin derivatives namely 5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)penta-2,4-dien-1-one (P1) and 5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)pent-2-en-1-one (P2) has been investigated using DFT quantum chemical approach. From the results and findings of the present study, it can be concluded that P1 and P2 are good inhibitors for the corrosion of mild steel in HCl solution. The inhibitory potentials of the inhibitors are due to the transfer of electron from the inhibitor to Fe in mild steel or vice versa. From experimental and theoretical data, the trend for the variation of the inhibition efficiencies of the compounds is P1 > P2. We emphasized also that benzodioxol ring, the two double bonds for P1 (respectively only one double bond for P2), pyridine ring, and oxygen atom of the carbonyl group are the possible active adsorption sites. Therefore, the use of quantum chemical parameters is appropriate in modelling the inhibitory of the studied piperidin based molecules.

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