



Density Functional Theory Investigations for the adsorption of some Oxadiazole Derivatives on Mild Steel

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ABSTRACT

Two oxadiazole derivatives namely 2,5-bis(4-methylphenyl)-1,3,4-oxadiazole (Inh-1) and 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole (Inh-II) were investigated as corrosion inhibitors for mild steel using density functional theory (DFT) at B3LYP/6-31G(d,p) 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), the energy gap(ΔE), hardness (η), Softness(S), dipole moment(μ), electron affinity(A), ionization potential(I), the absolute electronegativity (χ), the fraction of electron transferred (ΔN), electrophilicity index(ω) and the back-donation($\Delta E_{\text{Back-donation}}$) have been calculated and discussed. The local reactivity has been analysed through the Fukui and condensed softness indices in order to predict both the reactive centres and to know the possible sites of nucleophilic and electrophilic attacks. The theoretical conclusions were found to be consistent with the experimental data reported.

Keywords: Oxadiazoles, quantum chemical descriptors, reactivity, DFT, Fukui function, softness indices, electrophilicity index.

1. INTRODUCTION

The degradation of materials' properties due to interactions with their environment is called Corrosion. Corrosion phenomena of mild steel exist widely in various industrial fields, resulting in huge economic losses and many potential safety questions [1, 2]. The study of corrosion processes and their inhibition by organic compounds is a very active field of research [3]. Organic compounds, which can donate electrons to unoccupied d orbital of metal surface to form coordinate covalent bonds and can also accept free electrons from the metal surface by using their anti bonding orbital to form feedback bonds, constitute excellent corrosion inhibitors. Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media [4, 5]. It has been commonly recognized that organic inhibitor usually promotes formation of a chelate on the metal surface, which includes the transfer of electrons from the organic compounds to metal, forming coordinate covalent bond during such chemical adsorption process [6]. In this way, the metal acts as an electrophile, whereas the nucleophile centers of inhibitor molecule are normally hetero atoms with free electron pairs which are readily available for sharing, to form a bond. Many efficient inhibitors are heterocyclic organic compounds consisting of a π -system and / or oxygen, nitrogen, phosphorus or sulphur

hetero atoms [7-9]. The planarity and the lone electron pairs in the hetero atoms are important features that determine the adsorption of molecules on the metallic surface [10].

The inhibition efficiency has been closely related to the inhibitor adsorption abilities and the molecular properties for different kinds of organic compounds [11-13]. The adsorption of these compounds is influenced by the electronic structure of the inhibiting molecule [14] and also by the steric factors, aromaticity and electron density at the donor atoms [15]. Free electron pairs on hetero atoms or π electrons are readily available for sharing to form a bond and act as nucleophile centres of inhibitor molecules and greatly facilitate the adsorption process over the metal surface, whose atoms act as electrophiles [16]. The reactive ability of the inhibitor is closely linked to their frontier molecular orbital (FMO), including highest occupied molecular orbital, HOMO, and lowest unoccupied molecular orbital, LUMO, and the other parameters such as hardness and softness. Quantum chemical studies have been successfully performed to link the corrosion inhibition efficiency with molecular orbital (MO) energy levels for some kinds of organic compounds [17, 18]. Recently the effectiveness of an inhibitor molecule has been related to its spatial as well as electronic structure [19, 20].

M Lebrini *et al.* have studied the inhibiting effects of some oxadiazole derivatives on the corrosion of mild steel in perchloric acid solution [21]. Joseph Raj *et al.* have investigated the effect of some oxadiazole derivatives on the corrosion inhibition of brass in natural seawater [22]. A new class of corrosion inhibitors of mild steel in acidic media on the substituted 1,3,4-oxadiazoles was studied by bentiss *et al.* [23]. Although experimental work of M. Benabdellah, *et al.* [24] provide valuable information on the corrosion inhibition efficiency of 2,5-Bis(4-methylphenyl)-1,3,4-oxadiazole (Inh-I) and 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole (Inh-II), a deep understanding of the inhibition property remain unclear. To date, however, no study has been performed to investigate the corrosion inhibition efficiency of Inh-II > Inh-I by using quantum chemical calculations. The aim of the present work is to correlate the clear relationship between the experimentally determined inhibition efficiencies with the quantum chemical parameters of the investigated inhibitors.

The analyzed inhibitive properties are the molecular structure, the dipole moment, E_{HOMO} , E_{LUMO} , energy gap (ΔE), and those parameters that give valuable information about the reactive behavior: electronegativity (χ), global hardness (η) and the fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN) and the back-donation ($\Delta E_{\text{Back-donation}}$). The local reactivity has been analyzed by means of the Fukui indices, since they indicate the reactive regions, in the form of the nucleophilic and electrophilic behavior of each atom in the molecule. Results obtained showed that the inhibition efficiency of Inh-II > Inh-1. It is well correlated with the experimental results. From the calculations we have explained which adsorption site is favoured to bind to the metal surface.

2. MATERIAL AND METHODS

2.1. Quantum-chemical calculation

Among quantum chemical methods for evaluation of corrosion inhibitors, density functional theory (DFT) has shown significant promise and appears to be adequate for pointing out the changes in electronic structure responsible for inhibitory action [25]. In order to explore the theoretical-experimental consistency, quantum chemical calculations were performed with complete geometry optimizations using standard Gaussian-03 software package [26]. Geometry optimization were carried out by B3LYP functional at the 6-31G (d,p) basis set [27]. This basis set provided accurate geometry and electronic properties of a wide range of organic compounds [28]. Recently, Density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/surface mechanism and to describe the structural nature of the inhibitor in the corrosion process [29, 30]. Furthermore, DFT

is considered a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data. The results of the geometry optimization of the compounds Inh-I and Inh-II are presented in Figure 1.

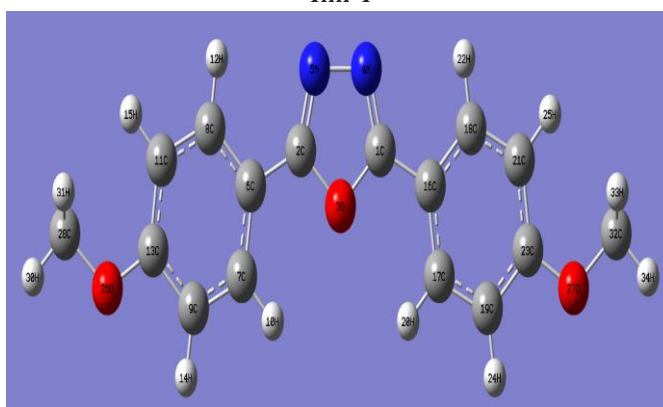
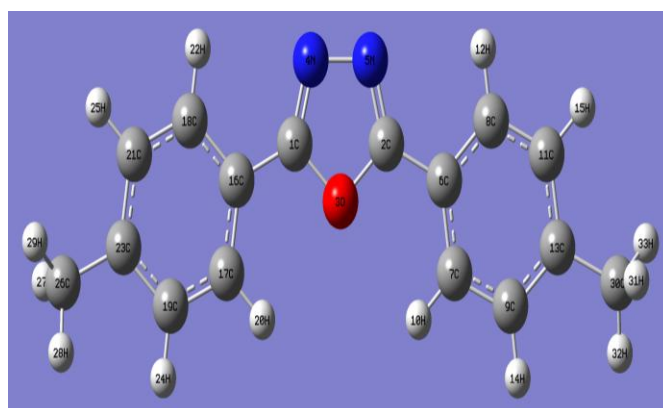
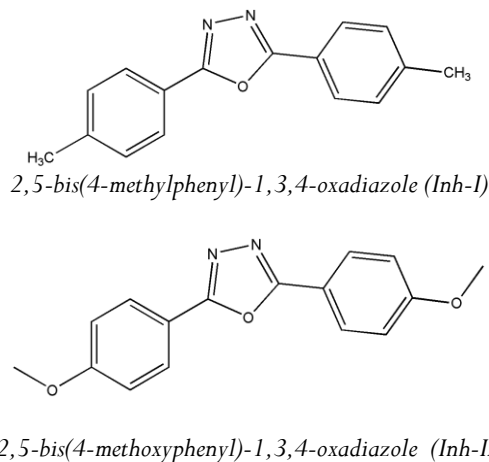


Figure 1. Optimized molecular structure of Inh-I and Inh-II by B3LYP/6-31G (d,p)

Density functional theory (DFT) has become an attractive theoretical method because it gives exact basic vital parameters for even huge complex molecules at low cost [31, 32]. It has been quite successful in providing theoretical basis for popular qualitative chemical concepts like electronegativity (χ),

hardness (η), softness(S) and local ones such as Fukui function, $F(r)$ and local softness, $s(r)$. The basic relationship of the density functional theory of chemical reactivity is precisely, the one established by Parr, Donnelly, Levy and Palke [33], that links the electronic chemical potential of DFT with the first derivative of the energy with respect to the number of electrons, and therefore with the negative of the electronegativity χ .

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r)} = -\chi \quad (1)$$

Where, μ is the electronic chemical potential, E is the total energy, N is the number of electrons, and $v(r)$ is the external potential of the system.

Hardness (η) has been defined within the DFT theory as the second derivative of the total energy with respect to N at $v(r)$ property which measures both the stability and reactivity of the molecule[34].

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

According to Koopman's theorem [35] the ionization potential (I) and electron affinity (A) are related to E_{HOMO} and E_{LUMO} by the following equation.

$$I = -E_{\text{HOMO}} \quad (3)$$

$$A = -E_{\text{LUMO}} \quad (4)$$

These quantities are related to the electronegativity(χ) and the global hardness(η) of the molecule using the following relations[36].

$$\chi = \frac{I+A}{2} \quad (5)$$

$$\eta = \frac{I-A}{2} \quad (6)$$

The global softness(S) is the inverse of the global hardness [37].

$$S = \frac{1}{\eta} = \frac{2}{I-A} \quad (7)$$

In the chemical reactivity theory, the parameters like electronegativity, hardness and softness have proved to be very useful quantities. The electronegativity of the inhibitor molecules is lower than the bulk Iron. Hence, electron move from the molecules with lower electronegativity (inhibitor compound) toward that of a higher value (metal surface) until the equilibrium in chemical potential is reached.

The global electrophilicity index (ω), introduced by Parr [38] and calculated using the electronic chemical potential and chemical hardness is given by

$$\omega = \frac{\mu^2}{2\eta} \quad (8)$$

According to the definition, this index measures the propensity of chemical species to accept electrons [39]. A good, more reactive, nucleophile is characterized by lower value of ω ; and conversely a good electrophile is characterized by a high value of ω . This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

For a reaction of two systems with different electronegativities (as a metallic surface and an inhibitor molecule) the following mechanism will take place: the electronic flow will occur from the molecule with the lower electronegativity towards that of higher value, until the chemical potentials are the same. The number of electron transferred (ΔN) from the inhibitor molecule to the metal surface can be calculated using the following equation [40].

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \quad (9)$$

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, the theoretical value for the electronegativity of bulk iron was used $\chi_{Fe}=7.0$ eV and a global hardness of $\eta_{Fe}=0$ by assuming that for a metallic bulk $I=A$ because they are softer than the neutral metallic atoms [41].

The local selectivity descriptors are often described in terms of condensed Fukui function which indicated the centre in the molecule on which certain types of reactivities are most likely to occur. Fukui functions provide information to relate to the atoms in a molecule that have a higher tendency to either lose or accept an electron or pair of electrons. The change in electron density is the nucleophilic $f^+(r)$ and electrophilic $f^-(r)$ Fukui functions, which can be calculated using the finite difference approximation as follows[42].

$$f_k^+ = q_{N+1} - q_N \quad (10)$$

$$f_k^- = q_N - q_{N-1} \quad (11)$$

Where, q_N , q_{N+1} and q_{N-1} are the electronic population of the atom k in neutral, anionic and cationic systems.

Condensed softness indices allowing the comparison of reactivity between similar atoms of different molecules can be calculated easily starting from the relation between the Fukui function $f(r)$ and the local softness $s(r)$ [43].

$$s(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)} \left(\frac{\partial N}{\partial \mu} \right)_{v(r)} = f(r)S \quad (12)$$

From this relation, one can infer that local softness and Fukui function are closely related, and they should play an important role in the field of chemical reactivity.

According to the simple charge transfer model for donation and back-donation of charges proposed recently by Gomez et al., [44] 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.

$$\Delta E_{\text{Back-donation}} = -\frac{\eta}{4} \quad (13)$$

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 back-donation from the molecule, is energetically 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.

3. RESULTS AND DISCUSSION

3.1. Global molecular reactivity

The inhibition effect of inhibitor 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 towards the donation of electron by a molecule [45].

High values of E_{HOMO} have a 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. 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. The frontier molecular orbital diagrams of Inh-I and Inh-II are represented in figure 3. Table 1 represents the calculated energy levels in (eV) of the HOMO, LUMO, energy gap and dipole moment of the investigated molecules.

Table 1. Global chemical reactivity indices for Inh-I and Inh-II calculated using B3LYP/6-31G (d,p)

Parameters	Inh-I	Inh-II
E (au)	-802.886345	-953.296893
E_{HOMO} (eV)	-5.9227	-5.5341
E_{LUMO} (eV)	-1.4801	-1.2313
Energy gap(ΔE) (eV)	4.4426	4.3028
Dipole moment(μ)D	3.7202	1.7496

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 [46]. 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 [47]. The E_{HOMO} for the two compounds follow the order Inh-II > Inh-I, which implies that the molecule which has the highest tendency to donate electrons is Inh-II. This is in agreement with the experimentally determined inhibition efficiency.

Table 2. Quantum chemical descriptors for Inh-I and Inh-II calculated using B3LYP/6-31G (d,p).

Parameters	Inh-I	Inh-II
Ionization potential (I) /(eV)	5.9227	5.5341
Electron affinity (A) /(eV)	1.4801	1.2313
Global Hardness(η) / eV	2.2213	2.1514
Electronegativity(χ) (eV)	3.7014	3.3827
Electrophilicity (ω)	3.08386	2.6593
Chemical Potential (μ)	-3.7014	-3.3827
Global softness(S)	0.450186	0.464813

Energy gap (ΔE) is an important parameter as a function of reactivity of the inhibitor molecule towards 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 [48]. A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule [49]. In our study,

the trend for the (ΔE) values follows the order Inh-II < Inh-I, which suggests that Inh-II has the highest reactivity in comparison to the other compound Inh-I and would therefore likely interact strongly with the metal surface.

There is lack of agreement in the literature on the correlation between the dipole moment and inhibition efficiency [50]. It is shown from the calculations that there was no obvious correlation between the values of the dipole moment with the trend of inhibition efficiency obtained experimentally.

Ionization energy is a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of the atoms and molecules [51]. The low ionization energy 5.5341(eV) of Inh-II indicates the high 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 [52]. It is shown from the calculations that Inh-II has the least value of global hardness 2.1514(eV) and the highest value of global softness is expected to have the highest inhibition efficiency. 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 [53]. Inh-II with the softness value of 0.464813 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 [54], the molecule Inh-I with a high electronegativity quickly reaches equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency. The table 2 shows the order of electronegativity as Inh-I>Inh-II. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order Inh-II>Inh-I. The 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 from the environment [55]. In our present study, Inh-II is the strongest nucleophile while Inh-I is the strongest electrophile.

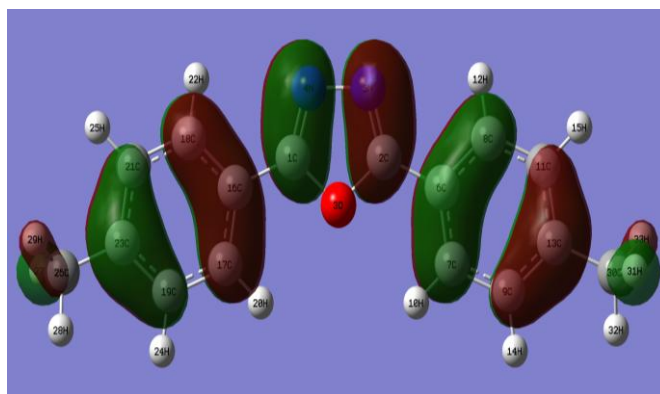
The number of electrons transferred (ΔN) was also calculated and tabulated in Table 3. Values of ΔN show that the

inhibition efficiency resulting from electron donation agrees with Lukovits's study [39]. 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: Inh-II>Inh-I. 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 (Inh-II), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (Inh-I).

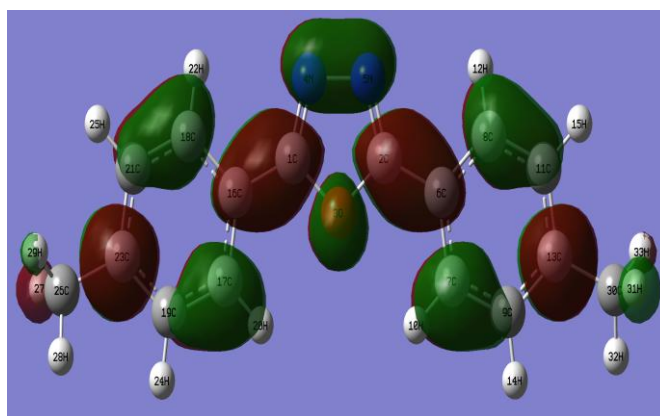
Table 3. The number of electron transferred (ΔN) and ΔE back donation (eV) calculated for Inh-I and Inh-II

Parameters	Inh-I	Inh-II
Transferred electrons fraction (ΔN)	0.74249	0.840685
ΔE back-donation/ (eV)	-0.55532	-0.53785

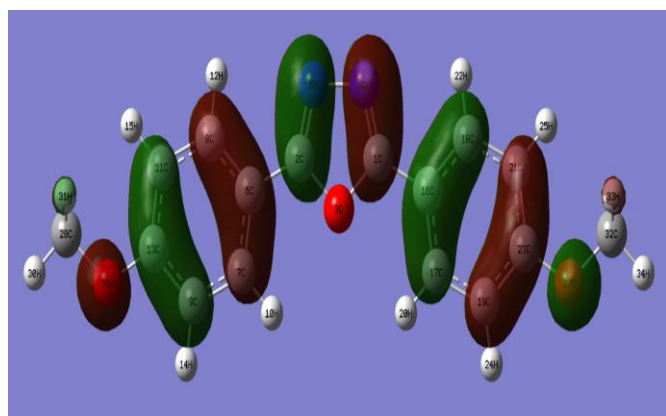
In Table 3, the calculated $\Delta E_{back-donation}$ values for the inhibitors are listed. The order followed is: Inh-II>Inh-I, which indicates that back-donation is favoured for the Inh-II, which is the best inhibitor.



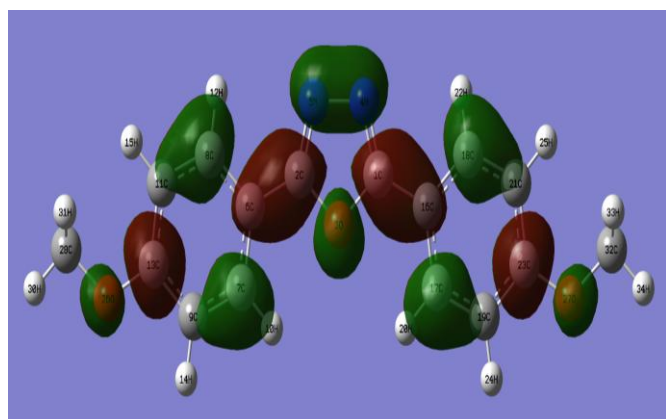
HOMO of Inh-I



LUMO of Inh-I



HOMO of Inh-II



LUMO of Inh-II

Figure 2. Frontier molecular orbital diagrams of Inh-I and Inh-II by B3LYP/6-31G (d,p)

The use of Mulliken population analysis to estimate the adsorption centres of inhibitors has been widely reported and it is mostly used for the calculation of the charge distribution over the whole skeleton of the molecule [56]. There is a general consensus by several authors that the more negatively charged heteroatom, is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction. It is important to consider the situation corresponding to a molecule that is going to receive a certain amount of charge at some centre and is going to back donate a certain amount of charge through the same centre or another one[44]. Parr and Yang proposed that larger value of Fukui function indicate more reactivity [27]. Hence greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule.

The local reactivity of molecule Inh-I and Inh-II is analyzed by means of the condensed Fukui function. The condensed Fukui function and local softness indices allow one distinguish each part of the molecule on the basis of its distinct chemical behavior [57] due to the different substituted functional group. The f_k^+ , measures the changes of density when the molecules gains electrons and it corresponds to reactivity with respect to nucleophilic attack. On the other hand, f_k^- corresponds to

reactivity with respect to electrophilic attack or when the molecule loss electrons. For electrophilic attack the most reactive site of Inh-I and Inh-II is on the N(5)atoms and for nucleophilic attack the most reactive site is C(2) in Inh-I and C(13) in Inh-II. The electrophilic and nucleophilic attacks of molecule Inh-I and Inh-II are tabulated in table 4 and 5.

Table 4. Fukui and local softness indices for electrophilic and nucleophilic attacks in Inh-I atoms calculated from Mulliken atomic charges.

Atom	f^-	f^+	s_k^-	s_k^+
1 C	0.03383	0.061893	0.0152298	0.0278633
2 C	0.03383	0.061894	0.0152298	0.0278638
3 O	0.021531	0.048561	0.009693	0.0218615
4 N	0.078777	0.035311	0.0354643	0.0158965
5 N	0.078778	0.035309	0.0354648	0.0158956
6 C	-0.014465	0.009912	-0.006512	0.0044622
7 C	0.03313	0.028687	0.0149147	0.0129145
8 C	0.031137	0.020411	0.0140174	0.0091887
9 C	0.019532	0.003919	0.008793	0.0017643
10 H	0.035872	0.035954	0.0161491	0.0161859
11 C	0.015236	0.008791	0.006859	0.0039575
12 H	0.043691	0.045359	0.0196691	0.0204199
13 C	0.012319	0.020958	0.0055458	0.0094349
14 H	0.051133	0.052006	0.0230194	0.0234124
15 H	0.05204	0.05445	0.0234277	0.0245126
16 C	-0.014467	0.009915	-0.006513	0.0044636
17 C	0.033133	0.028689	0.014916	0.0129154
18 C	0.031132	0.020411	0.0140152	0.0091887
19 C	0.01955	0.003889	0.0088011	0.0017507
20 H	0.035875	0.035952	0.0161504	0.0161851
21 C	0.015232	0.008809	0.0068572	0.0039657
22 H	0.043689	0.045359	0.0196682	0.0204199
23 C	0.012306	0.020967	0.00554	0.0094390
24 H	0.051128	0.052011	0.0230171	0.0234146
25 H	0.052036	0.054451	0.0234259	0.0245131
26 C	-0.011248	-0.008401	-0.005064	-0.0037820
27 H	0.040613	0.042586	0.0182834	0.0191716
28 H	0.037754	0.031304	0.0169963	0.0140926
29 H	0.029896	0.032573	0.0134588	0.0146639
30 C	-0.011256	-0.008394	-0.005067	-0.0037789
31 H	0.040569	0.042599	0.0182636	0.0191775
32 H	0.03775	0.031362	0.0169945	0.0141187
33 H	0.02994	0.032502	0.0134786	0.0146319

Table 5. Fukui and local softness indices for electrophilic and nucleophilic attacks in Inh-II atoms calculated from Mulliken atomic charges.

Atom	f^-	f^+	s_k^-	s_k^+
1 C	0.026839	0.063836	0.0124751	0.0296718
2 C	0.026839	0.063834	0.0124751	0.0296708
3 O	0.016910	0.045862	0.0078553	0.0213172
4 N	0.068799	0.028549	0.0319787	0.0132699
5 N	0.068810	0.028549	0.0319791	0.0132699
6 C	-0.013063	0.001023	-0.006072	0.0004755
7 C	0.028533	0.035851	0.0132625	0.0166640
8 C	0.030487	0.020413	0.0141708	0.0094882

Continued...

9 C	0.016238	-0.013863	0.0075476	-0.0064437
10 H	0.033111	0.032865	0.0153904	0.0152761
11 C	0.014308	-0.027991	0.0066505	-0.0130106
12 H	0.041051	0.04229	0.019081	0.0196569
13 C	0.028527	0.090216	0.0132597	0.0419336
14 H	0.048691	0.052957	0.0226322	0.0246151
15 H	0.044796	0.046148	0.0208218	0.0214502
16 C	-0.013065	0.001025	-0.006073	0.0004764
17 C	0.028531	0.035852	0.0132616	0.0166645
18 C	0.030483	0.020415	0.0141689	0.0094892
19 C	0.016237	-0.013863	0.0075472	-0.0064437
20 H	0.033112	0.032864	0.0153909	0.0152756
21 C	0.014305	-0.027992	0.0066491	-0.0130110
22 H	0.041052	0.042289	0.0190815	0.0196565
23 C	0.028531	0.09022	0.0132616	0.0419355
24 H	0.048692	0.052956	0.0226327	0.0246146
25 H	0.044799	0.046145	0.0208232	0.0214488
26 O	0.046999	0.029933	0.0218457	0.0139133
27 O	0.047009	0.029926	0.0218504	0.0139099
28 C	-0.029902	-0.035846	-0.013899	-0.0166616
29 H	0.032385	0.03181	0.015053	0.0147857
30 H	0.041372	0.046648	0.0192302	0.0216826
31 H	0.032375	0.032235	0.0150483	0.0149832
32 C	-0.029909	-0.035838	-0.013902	-0.0166579
33 H	0.03238	0.031792	0.0150506	0.0147773
34 H	0.041369	0.046653	0.0192288	0.0216849
35 H	0.032385	0.032239	0.015053	0.0149851

4. CONCLUSION

The corrosion inhibition efficiencies of two Oxadiazole derivatives was investigated using density functional theory at B3LYP/6-31-G (d,p) basis set. Quantum chemical parameters such as E_{HOMO} , E_{LUMO} , energy gap(ΔE), hardness(η), Softness(S), electron affinity(EA), ionization potential(IE), the absolute electronegativity (χ), the fraction of electron transferred (ΔN), electrophilicity index(ω) and the back-donation($\Delta E_{\text{Back-donation}}$) were calculated. The inhibition efficiency of Inh-I and Inh-II obtained quantum chemically increase with the increase in E_{HOMO} , and decrease in energy gap (ΔE). Inh-II has the highest inhibition efficiency because it had the highest HOMO energy and ΔN values and lowest energy gap it was most capable of offering electrons and it could have a better performance as corrosion inhibitor. Fukui function shows the nucleophilic and electrophilic attacking sites in the investigated inhibitors. The Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

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