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# Quantum chemical study on inhibitory action of some substituted 1,3,4-oxadiazoles on mild steel

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#### ABSTRACT

Quantum chemical calculations have been employed for the inhibition efficiency of two substituted 1,3,4oxadiazoles namely, 2,5-bis(2-pyridyl)-1,3,4- oxadiazole (POX) and 2,5-bis(2-hydroxyphenyl)-1,3,4-oxadiazole (HPOX) on mild steel have been investigated theoretically using density functional theory (DFT) at the B3LYP/6-31G(d,P) basis set level in order to elucidate the different inhibition efficiencies and reactive sites of these compounds as corrosion inhibitors. The calculated quantum chemical parameters correlated to the inhibition efficiency are the frontier molecular orbital energies  $E_{HOMO}$  (highest occupied molecular orbital energy),  $E_{LUMO}$ (lowest unoccupied molecular orbital energy), energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ) and the other parameters including global hardness ( $\eta$ ), global softness (S), the absolute electronegativity ( $\chi$ ), the electrophilicity index ( $\omega$ ) and the fractions of electrons transferred ( $\Delta N$ ) from the inhibitor molecule to the metallic atom. The local reactivity has been analyzed through the condensed Fukui function and condensed softness indices using Mulliken population analysis. The calculated results are in agreement with the experimental data.

Keywords: Oxadiazoles, Corrosion inhibition, reactivity, DFT, Fukui function, softness indices.

#### INTRODUCTION

Corrosion of mild steel is an inevitable process that produces a deterioration of materials and their properties resulting in massive economic losses especially when it occurs in aggressive media like hydrochloric acid [1]. In view of the problems created by mild steel corrosion, several researches on the methods of inhibition of its corrosion have been reported and it has been established that the use of inhibitors is one of the best methods of the prevention of the corrosion of mild steel in acidic medium[ 2]. The study of corrosion processes and their inhibition by organic compounds is a very active field of research [3]. Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media [4]. Most of the organic inhibitors containing nitrogen, oxygen, sulfur atoms, and multiple bonds in their molecules facilitate adsorption on the metal surface [5,6]. Researchers conclude that the adsorption on the metal surface depends mainly on the physicochemical properties of the inhibitor, such as the functional group, molecular electronic structure, electron density at the donor atom,  $\pi$  orbital character and the molecular size [7]. The planarity and the lone electron pairs in the hetero atoms are important features that determine the adsorption of molecules on the metallic surface [8]. Quantum chemical calculations have been widely used to study reactive mechanism and also an effective tool in the analysis and

elucidation of many experimental observations. They have been proved to be a very powerful tool for studying corrosion inhibition mechanism [9,10].

Substituted 1,3,4-Oxadiazoles derivatives are an important class of heterocyclic compounds, which play a pivotal role in a wide range of biological activities including antitubercular, antifungal, cytotoxic and ulcerogenic activities[11]. They have attracted considerable attention in the recent years for their diverse antibacterial activity[12], anti-HIV activity[13] and anticancer agents[14]. In literature, a few reports have been presented on the use of oxadiazole and some of its derivatives as corrosion inhibitors in different media [15-17]. Although experimental work of Bentiss *et al.* [18] provide valuable information on the corrosion inhibition efficiency of 1,3,4-oxadiazoles namely, 2,5-bis(2-pyridyl)-1,3,4- oxadiazole (POX) and 2,5-bis(2-hydroxyphenyl)-1,3,4- oxadiazole (HPOX) a deep understanding of the inhibition property remain unclear. The objective of the present paper is to extend the study of Bentiss *et al.* [18] by analyzing the inhibition efficiency of POX and HPOX on theoretical chemical parameters such as the energy gap ( $\Delta E$ ) between  $E_{HOMO}$  and  $E_{LUMO}$ , dipole moment ( $\mu$ ), ionization potential (I), electron affinity (A), electronegativity ( $\chi$ ), global hardness ( $\eta$ ), softness (S), the global electrophilicity ( $\omega$ ), the fraction of electrons transferred ( $\Delta N$ ) and back donation( $\Delta E$ ). 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 behaviour of each atom in the molecule using DFT calculations.

### MATERIALS AND METHODS

#### 2.1 Quantum Chemical Calculation

In order to explore the theoretical-experimental consistency, quantum chemical calculations were performed using Gaussian-03 software package [19]. Among quantum chemical methods for evaluation of corrosion inhibitors, density functional theory, DFT has shown significant promise [20] and appears to be adequate for pointing out the changes in electronic structure responsible for inhibitory action. Complete geometrical optimizations of the investigated molecules are performed using density functional theory(DFT) with the Becke's three parameter exchange functional along with the Lee– Yang–Parr nonlocal correlation functional (B3LYP) [21-23] at 6-31G(d,p) basis set level. This calculations have been widely used to study reaction mechanisms [24]. They have also been proved to be a very powerful tool for studying inhibition of the corrosion of metals [25,26]. The chemical and optimized structures of the compounds studied are given in Fig 1. and Fig 2.



Figure 1. Names, molecular structure and the abbreviation of the inhibitors investigated



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Figure 2. Optimized structure of POX and HPOX calculated with the B3LYP/6-31G(d,p)

#### 2.2. Global and local reactivity descriptors

Density functional theory (DFT) [27] has been found to be successful in providing theoretical insights into the chemical reactivity and selectivity, in terms of popular qualitative chemical concepts like electronegativity ( $\chi$ ), hardness ( $\eta$ ), softness(S), electrophilicity index( $\omega$ ) and local reactivity descriptors 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 [28], that links the 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  $\chi$ .

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

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

Hardness ( $\eta$ ) has been defined within the DFT as the second derivative of the E with respect to N as v(r) property which measures both the stability and reactivity of the molecule [29].

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

where v(r) and  $\mu$  are, respectively, the external and electronic chemical potentials.

According to Koopman's theorem [30], ionization potential (I) and electron affinity (A) the electronegativity( $\chi$ ), global hardness( $\eta$ ) and softness (S), may be defined in terms of the energy of the HOMO and the LUMO.

Ionization potential (I) is defined as the amount of energy required to remove an electron from a molecule [31]. It is related to the energy of the  $E_{HOMO}$  through the equation:

$$\mathbf{I} = -\mathbf{E}_{\mathrm{HOMO}} \tag{3}$$

Electron affinity (A) is defined as the energy released when a proton is added to a system [31]. It is related to  $E_{LUMO}$  through the equation:

$$A = -E_{LUMO}$$
(4)

When the values of *I* and *A* are known, one can determine the electronegativity  $\chi$  and the global hardness( $\eta$ ).

The electronegativity is the measure of the power of an atom or group of atoms to attract electrons towards itself [32], it can be estimated by using the equation:

$$\chi = \frac{I+A}{2} \tag{5}$$

Chemical hardness ( $\eta$ ) measures the resistance of an atom to a charge transfer [33], it is estimated by using the equation:

$$\eta = \frac{I - A}{2} \tag{6}$$

Chemical softness (S) is the measure of the capacity of an atom or group of atoms to receive electrons [33], it is estimated by using the equation:

$$S = \frac{1}{\eta} \tag{7}$$

For a reaction of two systems with different electronegativities the electronic flow will occur from the molecule with the lower electronegativity (the organic inhibitor) towards that of higher value (metallic surface), until the chemical

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potentials are equal [34]. Therefore the fraction of electrons transferred ( $\Delta N$ ) from the inhibitor molecule to the metallic atom was calculated according to Pearson electronegativity scale [35]

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{\left[2(\eta_{Fe} + \eta_{inh})\right]} \tag{8}$$

Where  $\chi_{Fe}$  and  $\chi_{inh}$  denote the absolute electronegativity of iron and inhibitor molecule respectively  $\eta_{Fe}$  and  $\eta_{inh}$  denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of  $\chi_{Fe}$ =7.0 eV[36] and  $\eta_{Fe}$  = 0 by assuming that for a metallic bulk I = A [37] because they are softer than the neutral metallic atoms.

The electrophilicity is a descriptor of reactivity that allows a quantitative classification of the global electrophilic nature of a molecule within a relative scale. Parr *et al* [38] have proposed electrophilicity index as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index( $\omega$ ) as follows.

$$\omega = \frac{\mu^2}{2\eta} \tag{9}$$

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  $\mu$ ,  $\omega$ ; and conversely a good electrophile is characterized by a high value of  $\mu$ ,  $\omega$ . This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge  $\Delta N$  from the environment.

#### 2.3. Local molecular reactivity

The Fukui function provides an avenue for analyzing the local selectivity of a corrosion inhibitor [39]. Their values are used to identify which atoms in the inhibitors are more prone to undergo an electrophilic or a nucleophilic attack. The change in electron density is the nucleophilic  $f^+(\mathbf{r})$  and electrophilic  $f^-(\mathbf{r})$  Fukui functions, which can be calculated using the finite difference approximation as follows [40].

$$f_{k}^{+} = q_{N+1} - q_{N} \tag{10}$$

$$f_{k} = q_{N} - q_{N-1} \tag{11}$$

where  $q_{N_{1}}q_{N+1}$  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) [41]

$$s(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{\nu(r)} \left(\frac{\partial N}{\partial \mu}\right)_{\nu(r)} = f(r)S$$
(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.*, [42] 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 related to the hardness of the molecule, as indicated in the following expression.

$$\Delta E_{\text{Back-donation}} = -\frac{\eta}{4} \tag{13}$$

The  $\Delta E_{Back-donation}$  implies that when  $\eta > 0$  and  $\Delta E_{Back-donation} < 0$  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.

#### **RESULTS AND DISCUSSION**

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 [43]. Table 1 represents the quantum chemical parameters for the inhibitors POX and HPOX. The energy of the highest occupied molecular orbital ( $E_{HOMO}$ ) measures the tendency towards the donation of electron, by a molecule. 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 inhibitor 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. Frontier molecular orbital diagrams of POX and HPOX is represented in fig. 3.

Table 1. Quantum chemical parameters for POX and HPOX calculated using B3LYP/6-31G(d,p).

Parameters	POX	HPOX
E <sub>HOMO</sub> (eV)	-6.555	-5.719
E <sub>LUMO</sub> (eV)	-1.986	-1.389
Energy gap( $\Delta E$ ) (eV)	4.569	4.33
Dipole moment (Debye)	7.2799	2.6422

The energy of the HOMO (EHOMO) is a quantum chemical parameter which provides information about the electron donating ability of the molecule. The molecule with the highest EHOMO value often has the highest tendency to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy[44]. 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  $E_{HOMO}$  -5.719 (eV) of HPOX indicates the better inhibition efficiency.

The energy gap between the HOMO and the LUMO ( $\Delta E$ ) provides information about the overall reactivity of a molecule. As  $\Delta E$  decreases the reactivity of the molecule increases leading to increase in the inhibition efficiency of the molecule [45]. Low values of the ( $\Delta E = E_{LUMO} - E_{HOMO}$ ) gap will render good inhibition efficiencies since the energy to remove an electron from the last occupied orbital will be minimized [46]. 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 [47]. In our study, the trend for the ( $\Delta E$ ) values follows the order HPOX<POX, which suggests that inhibitor HPOX has the highest reactivity in comparison to the other compound POX and would therefore likely interact strongly with the metal surface.

The dipole moment ( $\mu$  in Debye) is another important electronic parameter which provides the information on the polarity and the reactivity indicator of the molecule. Literature survey reveals that several irregularities appeared in case of correlation of dipole moment with inhibitor efficiency [43]. In general, there is no significant relationship between the dipole moment values and inhibition efficiencies [48]. 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.

Table 2 summarized the important global chemical parameters. 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[49]. The low ionization energy 5.719 (eV) of HPOX 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 [50]. In our present study HPOX with low hardness value 2.165 (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 [51]. 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 [52]. HPOX with the softness value of 0.46189 has the highest inhibition efficiency.

Table 2.	Ouantum	chemical	parameters for	POX	and HPOX	calculated using	B3LYP/6-31G(d.p).
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Parameters	POX	HPOX
IE(eV)	6.555	5.719
EA(eV)	1.986	1.389
η (eV)	2.2845	2.165
S	0.43773	0.46189
χ (eV)	4.2705	3.554
ω	3.9915	2.9171
μ	-4.2705	-3.554

The table 2 shows the order of electronegativity as POX> HPOX. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order HPOX> POX. According to Sanderson's electronegativity equalization principle [53], POX with a high electronegativity and low difference of electronegativity quickly reaches equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency.

The number of electrons transferred ( $\Delta N$ ) and *back-donation*( $\Delta E$ ) was also calculated and tabulated in Table 3. Values of  $\Delta N$  show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [54]. 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: POX <HPOX. The results indicate that  $\Delta N$  values correlates strongly with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is associated with the best inhibitor (HPOX), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (POX).

#### Table 3. The number of electron transferred ( $\Delta N$ ) and $\Delta E_{\text{back donation}}$ (eV) calculated for inhibitor POX and HPOX.

Parameters	POX	HPOX
Transferred electrons fraction ( $\Delta N$ )	0.59739	0.79584
$\Delta E_{back-donation} / (eV)$	-0.57112	-0.54125



HOMO of POX



LUMO of POX



HOMO of HPOX



#### LUMO of HPOX

Figure 3. Frontier molecular orbital diagrams of POX and HPOX by B3LYP/6-31G(d,p)

There is a general consensus by several authors that the more negatively charged a heteroatom, is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction [55]. 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 [42].

#### **3.1. Local Selectivity**

The condensed Fukui functions and condensed local softness indices allow us to distinguish each part of the molecule on the basis of its distinct chemical behavior due to the different substituent functional groups. It is known

that the Fukui indices were widely used as descriptors of site selectivity for the soft-soft reactions [56]. Parr and Yang proposed that larger value of Fukui function indicate more reactivity [57]. Hence greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule. 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. The calculated Fukui functions for the inhibitor POX and HPOX are presented in Tables 4 and 5.

It can be noticed that the N(3) and N(4) atoms are the dominant sites susceptible for electrophilic attacks in POX and HPOX. These atoms have the highest values of  $f^-$  which attain 0.09778 in POX (Table. 4) and 0.07536 in HPOX (Table. 5).

On the other hand, the susceptible sites for nucleophilic attack in both the inhibitor POX and HPOX are H(14) and H(23). These sites present the highest values of  $f^+$  which attain 0.06832 in POX (Table.4) and 0.06471 in HPOX(Table.5). These results agree well with the analysis of the HOMO and LUMO densities which also predicted these sites as the most electron rich and deficient centers.

Table 4. Fukui and local softness indices for nucleophilic and electrophilic attacks on POX atoms calculated from Mulliken atomic charges ; maxima in bold.

Atom No	$f_k$ +	$f_k$	$s_k^+$	Sk
1 C	0.05145	0.03810	0.02252	0.01667
2 C	0.05145	0.03810	0.02252	0.01667
3 N	0.04095	0.09778	0.01793	0.04280
4 N	0.04095	0.09778	0.01792	0.04280
5 O	0.04796	0.03104	0.02099	0.01358
6 C	0.04143	0.00288	0.01813	0.00126
7 C	0.01889	0.03565	0.00827	0.01560
8 C	0.01079	0.01131	0.00472	0.00495
9 H	0.03621	0.03959	0.01585	0.01733
10 C	0.00694	0.02701	0.00304	0.01182
11 C	0.03884	0.02802	0.01699	0.01226
12 H	0.05959	0.05472	0.02608	0.02395
13 H	0.06337	0.05714	0.02774	0.02501
14 H	0.06832	0.06339	0.02991	0.02775
15 C	0.04143	0.00288	0.01813	0.00126
16 C	0.01889	0.03565	0.00827	0.01560
17 C	0.01079	0.01131	0.00473	0.00495
18 H	0.03621	0.03959	0.01585	0.01733
19 C	0.00694	0.02701	0.00304	0.01182
20 C	0.03884	0.02802	0.01699	0.01227
21 H	0.05959	0.05472	0.02608	0.02395
22 H	0.06337	0.05714	0.02774	0.02501
23 H	0.06832	0.06339	0.02990	0.02775
24 N	0.03922	0.02888	0.01716	0.01264
25 N	0.03922	0.02888	0.01716	0.01264

Atom No	$f_k$ +	$f_k$	$s_k^+$	sk
1 C	0.05957	0.03203	0.02752	0.01479
2 C	0.05957	0.03203	0.02752	0.01479
3 N	0.03646	0.07536	0.01684	0.03481
4 N	0.03646	0.07536	0.01684	0.03481
5 O	0.04123	0.02228	0.01904	0.01026
6 C	0.00974	-0.01181	0.00449	-0.00546
7 C	0.03206	0.02837	0.01481	0.01310
8 C	-0.00416	0.01317	-0.00192	0.00608
9 H	0.03378	0.03115	0.01560	0.01439
10 C	0.01622	0.01499	0.00749	0.00692
11 C	0.03828	0.02165	0.01768	0.01000
12 H	0.05516	0.05371	0.02547	0.02481
13 H	0.05909	0.05355	0.02729	0.02473
14 H	0.06471	0.05844	0.02989	0.02699
15 C	0.00974	-0.01181	0.00449	-0.00545
16 C	0.03206	0.02837	0.01481	0.01310
17 C	-0.00416	0.01317	-0.00192	0.00608
18 H	0.03378	0.03115	0.01560	0.01439
19 C	0.01622	0.01499	0.00749	0.00692
20 C	0.03828	0.02165	0.01768	0.01000
21 H	0.05516	0.05371	0.02548	0.02481
22 H	0.05909	0.05355	0.02729	0.02473
23 H	0.06471	0.05844	0.02989	0.02699
24 C	0.03006	0.04278	0.01388	0.01976
25 O	0.02014	0.04199	0.00930	0.01939
26 H	0.02826	0.03351	0.01305	0.01548
27 C	0.03006	0.04278	0.01388	0.01976
28 O	0.02014	0.04199	0.00930	0.01939
29 H	0.02826	0.03351	0.01305	0.01548

Table 5. Fukui and local softness indices for nucleophilic and electrophilic attacks in HPOX atoms calculated from Mulliken atomic charges ; maxima in bold.

#### CONCLUSION

The inhibition efficiency of two substituted 1,3,4-oxadiazoles namely, 2,5-bis(2-pyridyl)-1,3,4- oxadiazole (POX) and 2,5-bis(2-hydroxyphenyl)-1,3,4-oxadiazole (HPOX) has been investigated by utilizing quantum chemical approaches using the Density Functional Theory method. The quantum chemical results have provided information on the reactivity centers of the compounds which would likely interact with the metal surface. HOMO, LUMO and condensed Fukui functions analysis agree on the possible electron donating centers and the possible electron poor centers on the inhibitor molecules. The inhibition efficiency of POX and HPOX increase with the increase in  $E_{HOMO}$ , and decrease in energy gap ( $\Delta E$ ). HPOX has the highest inhibition efficiency because it had the highest HOMO energy and  $\Delta N$  values and it was most capable of offering electrons. It may be due to the presence of an electron releasing -OH group in the aromatic ring at the ortho position. The parameters like hardness( $\eta$ ), Softness(S), dipole moment( $\mu$ ), electron affinity(EA) ionization potential(IE), electronegativity( $\chi$ ) and the fraction of electron transferred ( $\Delta N$ ) confirm the inhibition efficiency in the order of HPOX >POX.

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