



Density functional theory calculations on corrosion inhibitory action of five azlactones on mild steel

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ABSTRACT

A theoretical study for five azlactones, i.e., 4-benzylidene-2-phenyl oxazol-5-one (AZ1), 4-(4-methoxy benzylidene)-2-phenyl oxazol-5-one (AZ2), 4-(4-hydroxy-3-methoxy benzylidene)-2-phenyl oxazol-5-one (AZ3), 4-(2-hydroxy benzylidene)-2-phenyl oxazol-5-one (AZ4) and 4-(2-nitro benzylidene)-2-phenyl oxazol-5-one (AZ5), was investigated using density functional theory (DFT) at the B3LYP/6-31G(d,p) basis set level through the relationship between their molecular and electronic structure. The calculated quantum chemical parameters correlated to the inhibition efficiency such as E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap (ΔE), dipole moment (μ), absolute hardness (η), absolute softness (S), the absolute electronegativity (χ), the fractions of electrons transferred from the inhibitor molecule to the metallic atom (ΔN) and the electrophilicity index (ω) were calculated. The local selectivity and reactivity has been analyzed through the Fukui function and local softness indices in order to compare the possible sites for nucleophilic and electrophilic attacks. The theoretical results are in well accordance with the experimental data reported.

Keywords: azlactones, corrosion inhibition, DFT, Fukui function, softness, reactivity.

INTRODUCTION

Corrosion of metals is a major issue in various industrial fields, resulting in huge economic losses [1, 2]. Several approaches are therefore employed to reduce the corrosion process of mild steel and one of these approaches is the use of corrosion inhibitor [3]. Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media [4–6]. A number of heterocyclic compounds containing nitrogen, oxygen, and sulfur either in the aromatic or long chain carbon system have been reported to be effective inhibitors [7, 8]. Organic compounds, which can donate electrons to unoccupied d orbital of the 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 [9]. Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity [10]. Density functional theory (DFT) [11,12] has proven to be an important tool in modern quantum chemistry because of its ability to include some effects of electron correlation at a greatly reduced computation cost. It also have provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes [13-17]. A variety of chemical concepts which are now widely used as descriptors of chemical reactivity, e.g., electronegativity [14] hardness or softness quantities etc. appear naturally within DFT. The Fukui function [16] represents the relative local softness of the electron gas, measures the local electron density/population displacements corresponding to the inflow of a single electron. 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 [18, 19].

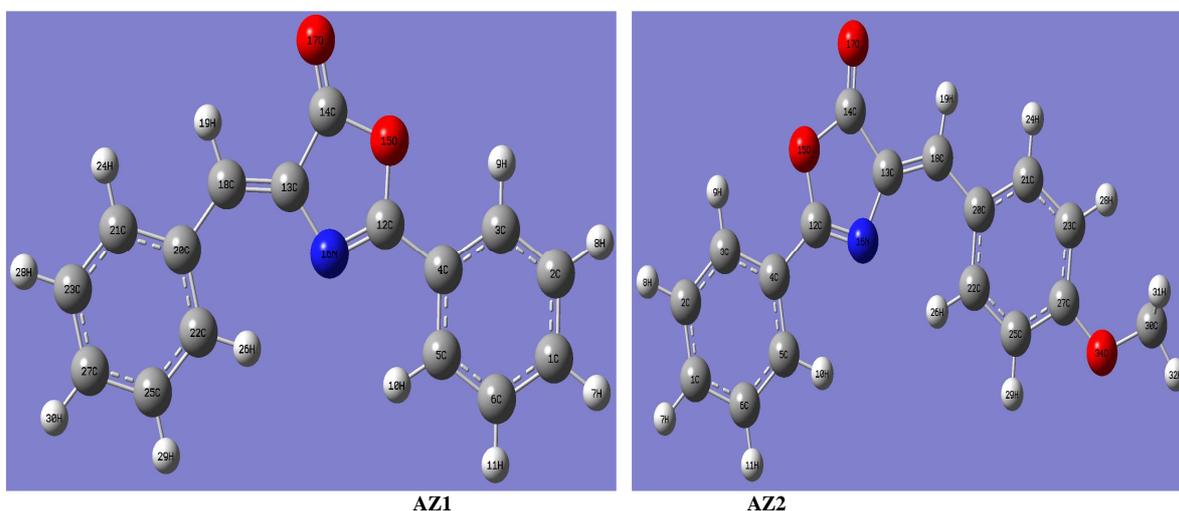
The azlactones are important synthones for the synthesis of several biologically active compounds[20]. They are known to exhibit antifungal[21], antibacterial[22] and anti-inflammatory activities. They are also of great importance to produce penicillin type of drug intermediates [23]. A series of 4-arylidene-2-phenyl-5(4H)-azlactones have been synthesized and the DFT calculations have been carried out by Mehtab Parveen *et.al.*[24].

The aim of the present work is to extend the experimental work of Parameswari *et.al.*[25] to ascertain whether the experimentally predicted order of inhibition efficiency are fully supported by the theoretically predicted quantum chemical parameters such as E_{HOMO} , E_{LUMO} , the energy gap (ΔE) between E_{HOMO} and E_{LUMO} , dipole moment (μ), ionization potential (I), electron affinity (A), electro negativity (χ), global hardness (η), softness (S), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and back donation(ΔE) of 4-benzylidene-2-phenyl oxazol-5-one (AZ1), 4-(4-methoxy benzylidene)-2-phenyl oxazol-5-one(AZ2), 4-(4hydroxy -3methoxy benzylidene)-2-phenyl oxazol-5-one (AZ3), 4-(2-hydroxy benzylidene)-2-phenyl oxazol-5-one (AZ4) and 4-(2-Nitro benzylidene)-2-phenyl oxazol-5-one (AZ5). The local selectivity and 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.

2. COMPUTATIONAL DETAILS AND CALCULATIONS

2.1 DFT Calculations

The present calculations have been performed at the B3LYP level of theory using Gaussian-03 series of program package [26]. The calculations were based on 6-31G (d,p) basis set. This method has been widely implemented to study the relationship between corrosion inhibition efficiency of the molecules and their electronic properties [27]. In order to establish correlation between experimental data and structural and electronic characteristics of the investigated inhibitors, the geometry of the molecules were optimized by the density functional theory(DFT)[11] with the Becke's three parameter exchange functional[28] along with the Lee- Yang-Parr correlation functional (B3LYP) [29]. The optimized structure of the investigated inhibitors are given in Fig 1.



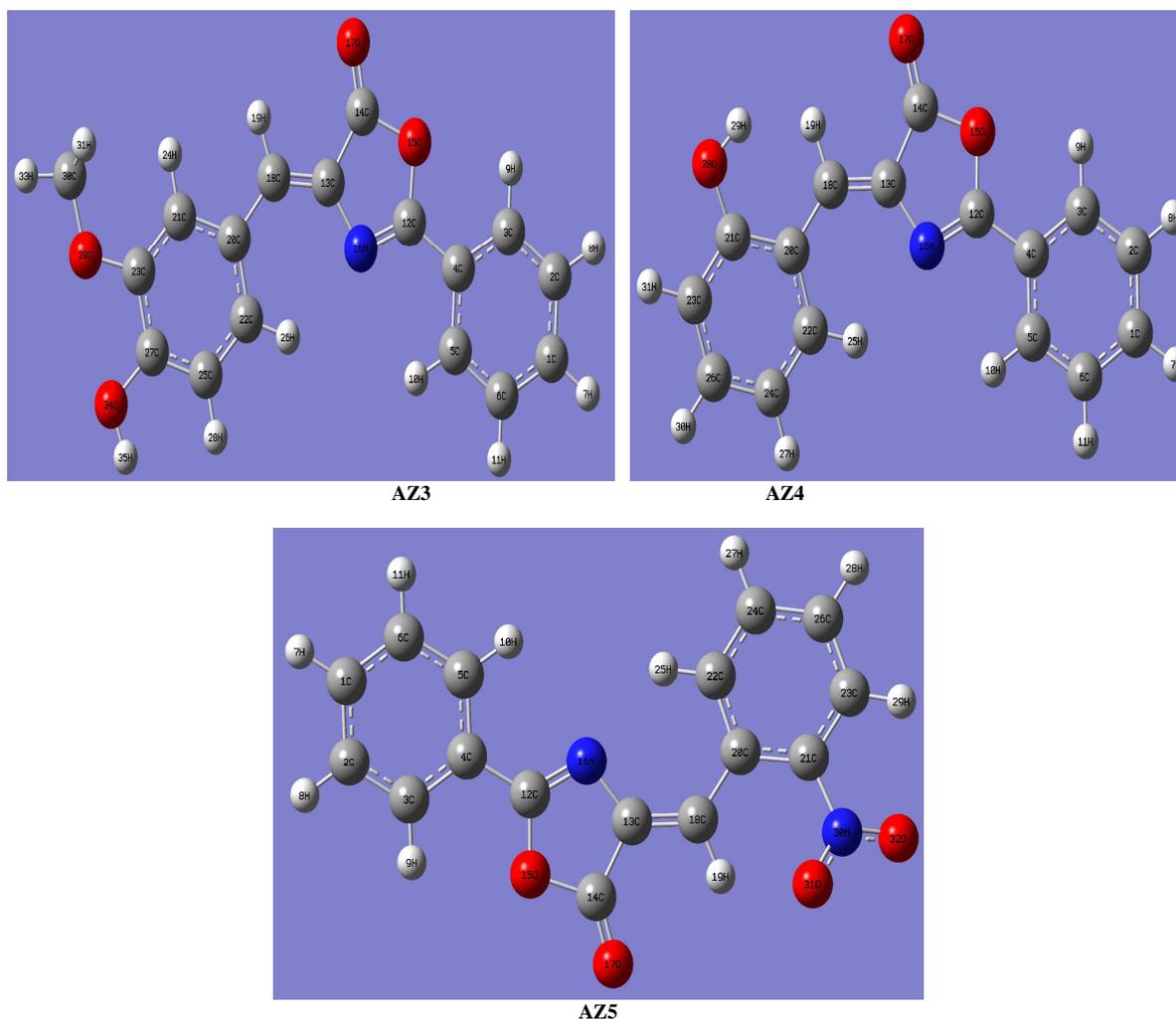


Figure 1. Optimized structure of the investigated inhibitors AZ1,AZ2,AZ3,AZ4 and AZ5 calculated with the B3LYP/6-31G(d,p)

2.2 Global quantities

The basic relationship of the density functional theory of chemical reactivity is precisely, the one established by Parr *et al.*, [30], 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 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 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 [31].

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

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

According to Koopman's theorem [32], ionization potential (I), electron affinity (A), the electronegativity (χ), global hardness (η) and softness (S), may be defined in terms of the energy of the HOMO and the LUMO.

Ionization potential (I) is related to the energy of the E_{HOMO} through the equation [33]:

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

Electron affinity (A) is [33] related to E_{LUMO} through the equation:

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

When the values of I and A are known, one can determine the electronegativity χ and the global hardness (η).

The electronegativity [34], can be estimated by using the equation:

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

Chemical hardness (η) measures the resistance of an atom to charge transfer [35], it is estimated by using the equation:

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

Chemical softness (S), the reverse of hardness [35], is estimated by using the equation:

$$S = \frac{1}{\eta} \quad (7)$$

During the interaction of the azlactones with the iron surface, electron flow from the lower electronegativity inhibitors to the higher electronegativity iron surface until the chemical potential becomes equalized [36]. The fraction of electrons transferred (ΔN) was calculated according to Pearson electronegativity scale [37].

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})} \quad (8)$$

The theoretical value of $\chi_{\text{Fe}}=7.0$ eV [38] and $\eta_{\text{Fe}} = 0$ is used assuming that for a metallic bulk $I = A$ [39] because they are softer than the neutral metallic atoms.

Parr *et al.*, [40] have defined electrophilicity index (ω) as follows.

$$\omega = \frac{\mu^2}{2\eta} \quad (9)$$

According to the definition, this index measures the propensity of chemical species to accept electrons. A good, more reactive, nucleophile is characterized by low 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.

Fukui functions were computed since it provides an avenue for analyzing the local selectivity of a corrosion inhibitor [41]. 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 $f^+(r)$ and electrophilic $f^-(r)$ Fukui functions, which can be calculated using the finite difference approximation as follows [42].

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

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

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 related 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.

RESULTS AND DISCUSSION

3.1 Frontier Molecular Orbital (FMO) Level Calculations

According to the frontier molecular orbital theory, chemical reactivity is a function of the interaction between the HOMO and LUMO levels of reacting species [45]. 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 inhibition efficiency. E_{LUMO} indicates the ability of the molecule to accept electrons. Frontier molecular orbital diagrams of the studied compounds are represented in fig. 2.

Table 1. Quantum chemical parameters for the studied molecules calculated using B3LYP/6-31G(d,p)

Parameters	AZ1	AZ2	AZ3	AZ4	AZ5
E_{HOMO} (eV)	-5.9521	-5.5909	-5.4726	-5.8574	-6.3603
E_{LUMO} (eV)	-2.4918	-2.2942	-2.3095	-2.5440	-2.7326
Energy gap (ΔE) (eV)	3.4603	3.2967	3.1631	3.3134	3.6277
Dipole moment (Debye)	3.5482	4.2006	3.7498	3.4883	7.6639

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 [46]. 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. From table 1 it is observed that E_{HOMO} for the five compounds follows the order; $AZ3 > AZ2 > AZ4 > AZ1 > AZ5$ which implies that AZ3 has the highest tendency to donate electrons.

The energy gap between the E_{HOMO} and E_{LUMO} energy levels of the molecules 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 [47]. Hard molecules have high HOMO-LUMO gap [48] and thus soft bases inhibitors are the most effective for metals [49]. The results as indicated in table 1 show that inhibitor AZ3 has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor than other molecules. It is shown from the calculation that there was no obvious correlation between the values of dipole moment with the trend of inhibition efficiency obtained experimentally. In the literature also there is a lack of agreement on the correlation between the dipole moment and inhibition efficiency [50,51]. Other computed quantum chemical properties such as ionization potential (I), electron affinity (A), electro negativity (χ), global hardness (η), softness (S), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and back donation (ΔE) are given in table 2.

Table 2. Quantum chemical parameters for AZ1,AZ2,AZ3,AZ4 and AZ5 calculated using B3LYP/6-31G(d,p) level of theory

Parameters	AZ1	AZ2	AZ3	AZ4	AZ5
IE(eV)	5.9521	5.5909	5.4726	5.8574	6.3603
EA(eV)	2.4918	2.2942	2.3095	2.5440	2.7326
η (eV)	1.73025	1.64835	1.58155	1.6567	1.81385
S (eV)	0.57795	0.60667	0.63229	0.60361	0.55131
χ (eV)	4.2220	3.94255	3.89105	4.2007	4.54645
ω	5.15107	4.71493	4.78653	5.32561	5.69788
μ	-4.2220	-3.94255	-3.89105	-4.2007	-4.54645

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 [52]. The low ionization energy 5.4726 eV of AZ3 indicates the high inhibition efficiency.

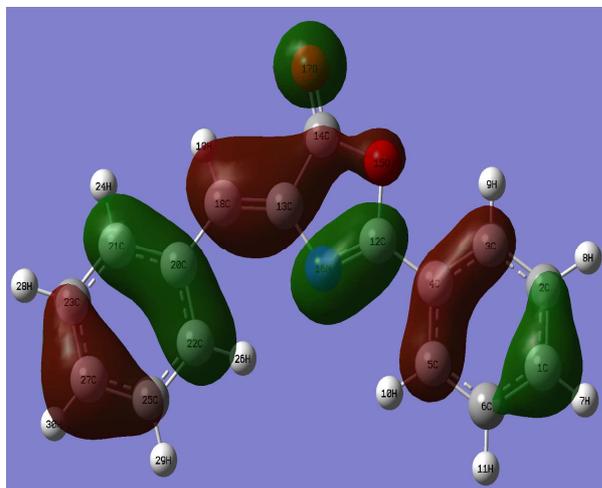
Hardness and softness are the basic chemical concepts, called global reactivity descriptors which have been theoretically justified within the framework of density functional theory (DFT)[11]. These are the important properties to measure the molecular stability and reactivity. It is apparent that the 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 [53]. In our present study AZ3 with low hardness value 1.58155 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 [54]. 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 [55]. AZ3 with the softness value of 0.63229 eV has the highest inhibition efficiency.

The table 2 shows the order of electronegativity as $AZ3 < AZ2 < AZ4 < AZ1 < AZ5$. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order $AZ3 > AZ2 > AZ4 > AZ1 > AZ5$. According to Sanderson's electronegativity equalization principle [56], 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.

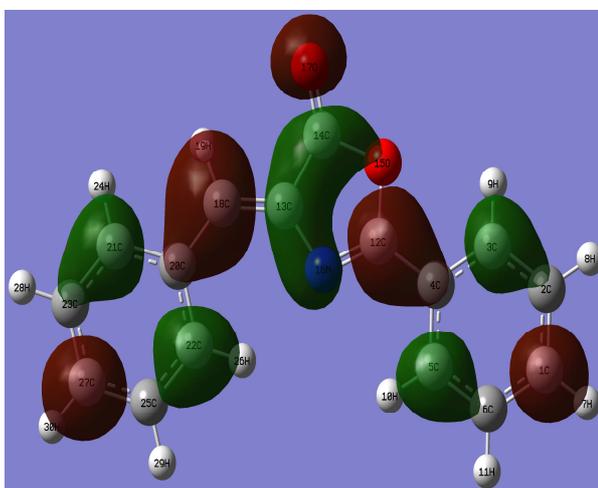
The number of electrons transferred (ΔN) and *back-donation*(ΔE) was also calculated and tabulated in Table 3. Values of ΔN show that the inhibition efficiency resulting from electron donation agrees with Lukovits' study [57]. If $\Delta N < 3.6$, the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface and it increases in the following order; $AZ3 > AZ2 > AZ4 > AZ1 > AZ5$. 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 (AZ3), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (AZ5).

Table 3. The number of electron transferred (ΔN) and ΔE back donation (eV) calculated for inhibitor AZ1, AZ2, AZ3, AZ4 and AZ5

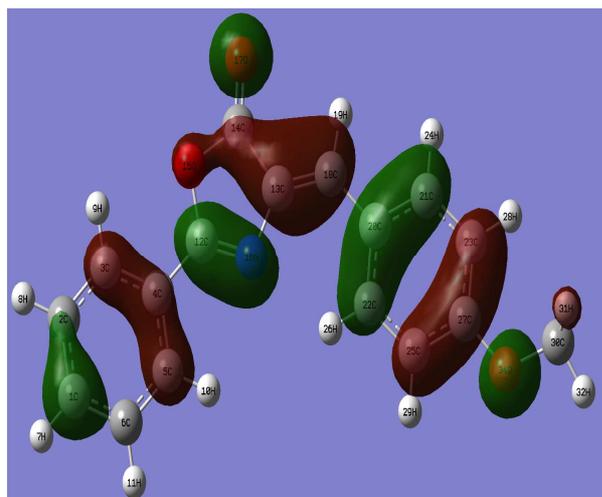
Parameters	AZ1	AZ2	AZ3	AZ4	AZ5
Transferred electrons fraction (ΔN)	0.80277	0.92743	0.98288	0.84484	0.67634
Back-donation ΔE / (eV)	-0.43256	-0.41209	-0.39539	-0.41417	-0.45346



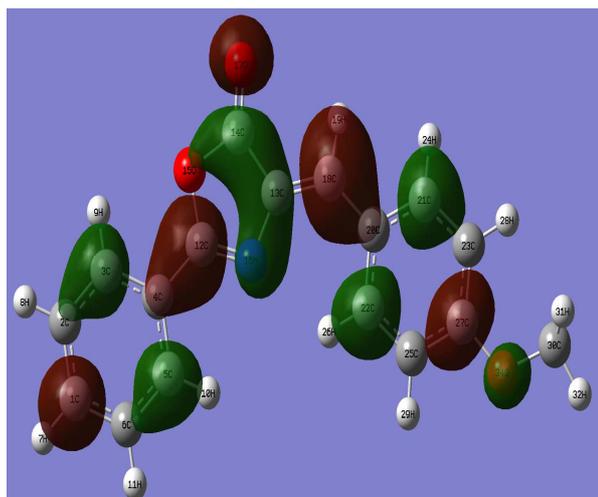
HOMO of AZ1



LUMO AZ1



HOMO of AZ2



LUMO of AZ2

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 [58]. 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 [45]. Parr and Yang proposed that larger value of Fukui function indicate more reactivity [16]. Hence greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule.

3.2 Local Selectivity

Fukui functions compute local reactivity indices that makes possible to rationalize the reactivity of individual molecular orbital contributions. The condensed Fukui function and local softness indices allow one distinguish each part of the molecule on the basis of its distinct chemical behaviour due to the different substituted functional group [59]. 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 highest Fukui Indices values for the studied inhibitors are presented in Table 4.

Table. 4 The highest Fukui indices vales calculated with B3LYP/6-31G(d,p) for the studied inhibitors

Inhibitor	Atom	f_k^+	f_k^-
AZ1	O(17)	0.08498	0.08286
	H(19)	0.09039	0.04468
	C(14)	0.07759	0.05755
AZ2	C(12)	0.33478	0.20381
	C(13)	0.25613	-0.14626
	N(16)	-0.12268	0.21446
AZ3	C(14)	0.07566	0.05168
	O(17)	0.08252	0.07626
	H(19)	0.08919	0.03236
AZ4	C(12)	0.33050	0.04233
	C(13)	0.26131	0.05079
	O(17)	0.01936	0.07134
AZ5	C(12)	0.05858	0.31635
	C(13)	0.06453	0.24560
	O(17)	0.08276	0.02138

According to fukui indices, the preferred sites for attack by a nucleophilic agent is near C(12) atom in the inhibitors AZ2 and AZ4, whereas the same is near H(19) in AZ1 and AZ3. In the case of AZ5 due to the presence of highly electron attracting NO₂ group the O(17) becomes nucleophilic attacking site.

The preferred site for electrophilic agents for AZ1, AZ3 and AZ4 is near O(17) atom and the same is in N(16) in the inhibitor AZ2 and C(12) in AZ5.

3.3 Reactivity

The azlactones under investigation having electron donating and electron withdrawing substituents in the aromatic ring system react with mild steel in various forms and inhibit corrosion in different range. The electron withdrawing NO₂ group of AZ5 decreases its softness to 0.55131 eV compared to the other inhibitors whereas the electron donating -OH and -OCH₃ of AZ3 increases the softness to 0.63229 eV. The chemical hardness 1.81385 eV of AZ5 with NO₂ as substituent shows its least reactivity in this series of compounds. The highest chemical potential -3.89105 eV of the compound with electron donating substituents in reference with -4.222 eV with no substituent and -4.54645eV of NO₂ substituted compound indicates the highest inhibition of AZ3.

CONCLUSION

1. The inhibitory properties of five azlactones has been elucidated using quantum chemical calculations based on density functional theory at B3LYP/6-31G(d,p) basis set level. The calculated electronic parameters involved in the activity of the inhibitors confirmed that the order of inhibition efficiency.
2. The inhibition efficiency increase with the increase in E_{HOMO} , and decrease in energy gap (ΔE). AZ3 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.
3. The parameters like hardness (η), Softness (S), electron affinity (EA) ionization potential (IE), electronegativity (χ) and the fraction of electron transferred (ΔN) confirm the inhibition efficiency in the order of AZ3 > AZ2 > AZ4 > AZ1 > AZ5.
4. Fukui function shows the nucleophilic and electrophilic attacking sites in the inhibitors.
5. Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the quantum chemical method employed here to study the inhibition of corrosion of metal surface and also revealed the reactivity of the azlactones under study.

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