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THEORETICAL MODELING OF IMINOISATIN DERIVATIVES AS CORROSION INHIBITORS OF STEEL IN ACID SOLUTION

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ABSTRACT

The effect of two iminoisatin derivatives [1-morpholinomethyl-3(1-N-dithiooxamide) iminoisatin (molecule 1)] and 1-diphenylaminomethyl-3(1-N-dithiooxamide) iminoisatin (molecule 2) on corrosion inhibition were theoretically investigated using quantum mechanical method. Their electronic parameters and quantum chemical descriptors that predict their adsorption and hence their inhibition efficiency were estimated using the DFT//B3LYP/6-31G (d) method. The results established a relationship between the quantum descriptors and corrosion inhibition efficiency, and also confirmed molecule 2 to be a better corrosion inhibitor and provide a guide to the synthesis of more efficient organic corrosion inhibitors.

Keywords: DFT, Iminosatin, Inhibition efficiency, Quantum descriptors.

INTRODUCTION

Corrosion refers to the gradual deterioration of the properties of materials, especially metals and alloys, when interacting with the environment (Stansbury and Buchanan, 2000). The marvel of corrosion is as old as the history of metals and is considered a threat that destroys the entire metallic structures and turns beauty into a beast. Our human development cannot exist without metals, and yet corrosion is an Achilles' heel. This has raised serious concerns as it costs enormous material losses and safety concerns (Nestor, 2004). Thus, reducing the rate of corrosion to the barest minimum has been the research effort of scientists and engineers. Both small and large organic molecules containing phosphorous oxygen, sulfur or nitrogen in their heterocyclic molecular structures have been widely known as organic inhibitors of corrosion in steel in acidic solutions (Raja *et al*., 2013; Kamal *et al*., 2014). Through the process of adsorption, organic molecules can reduce the rate of corrosion at the metal-solution phase (Mahendra *et al*., 2013), thereby forming a protective layer that reduces the rate of corrosion. The relationship between structure and adsorption property coupled with adsorption mechanisms of inhibitors are usually considered when searching for an efficient organic inhibitor. It is worthy to note that the adsorption of organic inhibitors mainly depends on their electronic and structural properties (Ogunyemi *et al*., 2020; Quraishi and Sharma, 2002). Using a computational chemistry methodology, the electronic and structural properties can be obtained theoretically. Although experimental works have been explicitly used to determine the inhibition efficiency correctly but this could sometimes be expensive and time consuming. Consequently, the use of theoretical methods has become a desirable approach to probe the inhibition efficiency of organic inhibitors towards the corrosion process since they may overcome disadvantages of trial and error of experimental approach (Zhao *et al*., 2014; Zhang *et al*., 2010). The effectiveness of corrosion inhibitors is closely linked to quantum chemical descriptors calculated from the DFT approach. Thus, the continuous advances in hardware and software has made theoretical methods powerful tool for assessing the corrosion inhibition efficiency and quite a numbers of quantum chemical modelling methods have been established to relate the inhibitory effectiveness of organic inhibitors with their molecular properties (Ogunyemi, *et al*., 2020). Therefore, this research is aimed at explaining and interpreting the experimental results of iminoisatin derivatives and establishing a correlation between inhibiting properties of molecules and their inhibitory efficiency (as shown in Figure 1) using a quantum mechanical approach. This approach probes molecular reactivity descriptors that characterize their inhibitory properties and further elucidate their electronic structures and reactivity toward prediction of their corrosion inhibition efficiency.

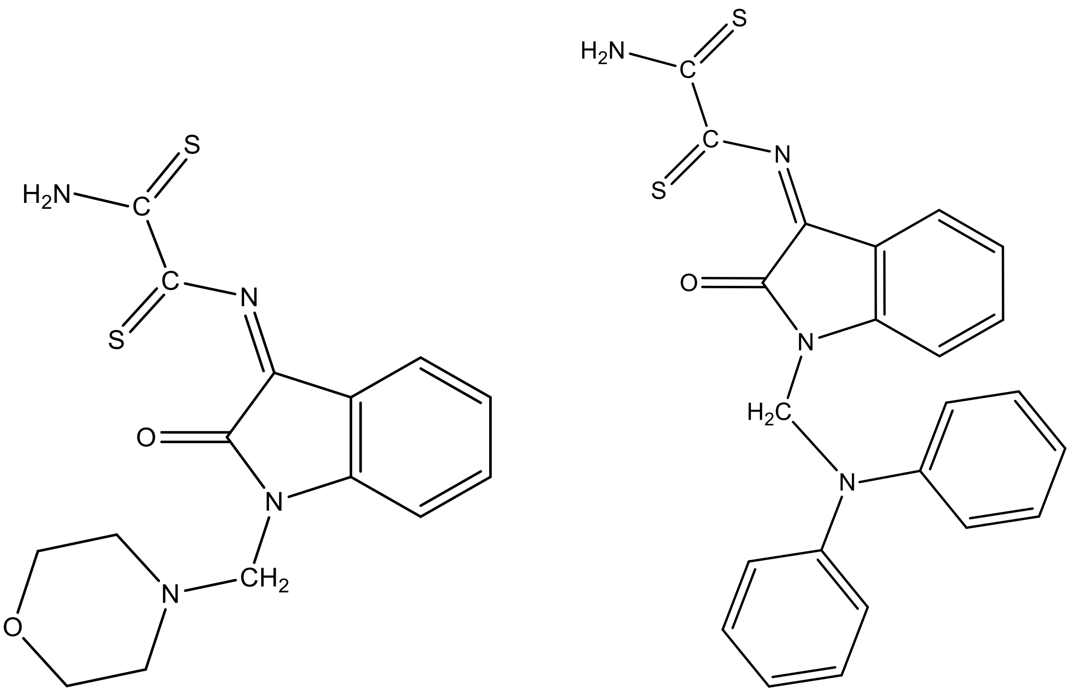

Figure1. The structures of iminoisatin derivatives: molecule 1 (left) and molecule 2 (right).

EXPERIMENTAL

Computational methodology

Molecular modeling techniques have provided a competitive alternative to interpret experimental data and ensure the predictability of new materials arising from industrial interests and developments. The optimization and energy calculations of the ground-state equilibrium geometry of the two iminoisatin derivatives were fully optimized using DFT/B3LYP (Becke, 1988; Lee *et al*., 1988) and 6-31G(d) basis set. During optimization, dihedral angle, bond angles and bond length were free from constraints. Their stationary points were examined to ensure real vibrational frequencies were arrived at, during the process of optimization. The molecular orbital energies; E_{HOMO} and E_{LUMO} levels were also calculated. The prediction of adsorption sites was possible through the determination of the frontier molecular orbitals (HOMO and LUMO) of the studied organic inhibitors. The electron affinity (EA) and ionization potential (IP) of the studied inhibitors were related to the E_{HOMO} and E_{LUMO} using Koopman's theorem (Pearson, 1988). These are clearly shown in equation 1 and 2:

$$IP = -E_{HOMO} \qquad (1)$$

$$EA = -E_{LUMO} \qquad (2)$$

The electronegativity (χ) and absolute hardness values of the organic inhibitors were calculated using equation 3 and 4 respectively (14). Meanwhile, softness, which is the inverse of hardness is also a quantum parameter calculated using 5.

$$\eta = \left(\frac{\delta\varepsilon^2}{\delta N^2}\right)_{v(r)} = \frac{E_{LUMO} + E_{HOMO}}{2} = \frac{IP - EA}{2} \qquad (3)$$

$$\chi = -\mu = \left(\frac{\delta\varepsilon}{\delta N}\right)_{v(r)} = -\frac{E_{LUMO} + E_{HOMO}}{2} = \frac{IP + EA}{2} \qquad (4)$$

$$S = \frac{1}{\eta} \qquad (5)$$

The three quantum parameters of organic inhibitors: softness, electronegativity and hardness are very helpful in examining their chemical reactivity. Contact of a metal with an organic molecule establishes a flow of electrons flow between the two systems until their chemical potentials become equal. Electrons transferred (ΔN) was also calculated theoretically as reported in the literature (Parr,1983) using equation 6:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \qquad (6)$$

where χ_{Fe} and χ_{inh} represent the absolute electronegativities of iron (Fe) and organic inhibitor while η_{Fe} and η_{inh} represent the hardness of iron (Fe) and inhibitor respectively. The theoretical absolute electronegativity value of Fe $(\chi_{Fe} = 7$ eV/mole) and theoretical absolute hardness of iron $(\eta_{Fe} = 0\ eV/mole)$ were used to calculate the number of transferred electrons.

The electrophilicity index parameter of each of the molecules was estimated using equation 7 (Parr *et al.*, 1999). This property measures the stabilization energy when charges are transferred to a system from the environment. It also measures the tendency of chemical species to accept electrons.

$$\omega = \frac{\mu^2}{2\eta} \qquad (7)$$

When the values of μ and ω are low, it shows that inhibiting molecules is a more reactive nucleophile while high values depict a more reactive electrophile.

RESULTS AND DISCUSSION

The corrosion inhibition efficiency of iminoisatin derivatives: (molecule 1 and 2), were theoretically investigated theoretically using DFT/B3LYP/6-31G*. the calculated quantum parameters of the optimized structures of the studied iminoisatin derivatives (Fig. 2), such as the E_{HOMO}, E_{LUMO}, Separation energy ΔE, dipole moment (DM), Log P, solvation energy (Esolv), Ovality, Electron Affinity (EA), Ionization Potential (IP), global electrophilicity (*ω*), softness (s), chemical hardness (η), electronegativity (χ), electronegativity (χ), molecular weight (MW), total energy of electron transfer ΔN and polarizability are shown in Table 1. Experimentally determined inhibition efficiency values for molecule 1 and 2, decreases in the following order: 84.4% for molecule 1 and 91% for molecule 2 (5). Figure 1 displayed above shows that the geometric structures of the iminoisatin derivatives presented in this work contain amino group. The E_{HOMO} measures the electron donating ability of an inhibitor. If the E_{HOMO} of an inhibitor is increased, the tendency for the inhibitor to donate electrons to the corresponding molecular orbital which is lower in molecular energy level becomes higher.

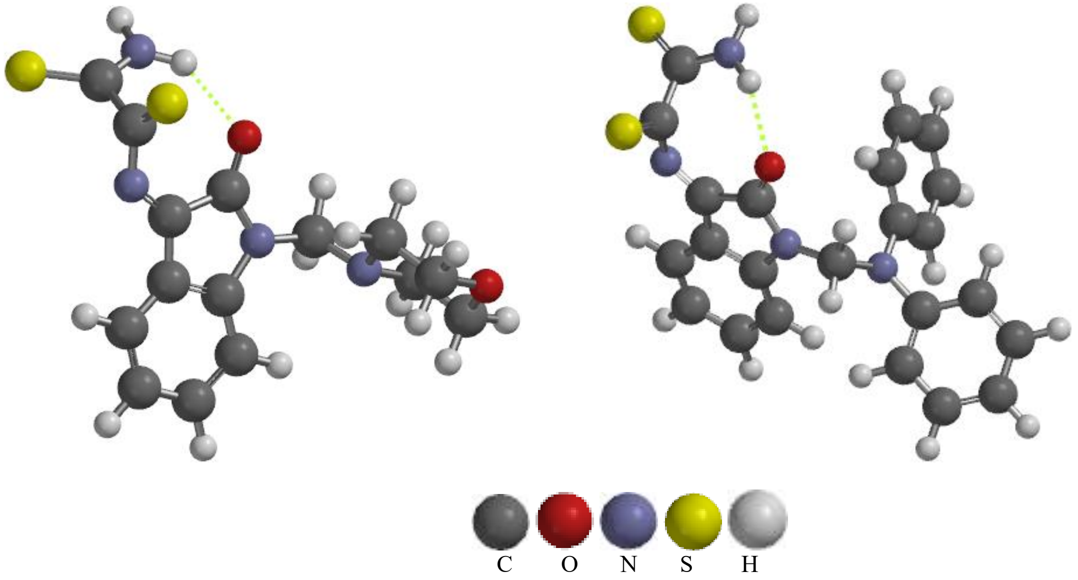

Figure2: Equilibrium geometry of the inhibitors molecules calculated by DFT/B3LYP/6-31G (d) methods.

Therefore, the enhancement of the electron transferring process of an inhibitor can improve the effectiveness and efficiency of an inhibiting molecule. The E_{HOMO} values of the studied molecules as shown in Table 1, follow the order; Molecule 2 > Molecule 1. This order clearly indicated that the highest value of E_{HOMO} (-5.59 eV) for Molecule 2, may be the best inhibitor to give electrons to the corresponding empty *d*-orbital of the metal ion. It is however worthy to note that, during electron transferring process between metal and inhibitor, electrons are not only donated to the empty *d*-orbital of the metal ion, and also the inhibiting molecules accept electrons from the *d*-orbital of the metal leading to formation of the feedback bond which is a function of E_{LUMO}. Thus accepting ability of the studied molecules from the metal ion was considered by estimating the E_{LUMO} values of Molecule 1 and Molecule 2. Table 1 shows that the E_{LUMO} values for Molecule 1 (-3.01 eV) and Molecule 2 (-2.99 eV) follow the order: Molecule > Molecule 1. Thus, Molecule 2 has a better tendency to accept electrons from the corresponding metal ion more than Molecule 1. The values of the molecular orbital energies (HOMO and LUMO) show that Molecule 2 could definitely have an improved adsorption and better inhibition efficiency than Molecule 1 on the surface of the metal surface.

The frontier molecular orbital density distribution examination of the studied iminoisatin derivatives (Figure 3) shows that electron density distribution on HOMO were localized on the amino group attached to the isatan and distributions on the LUMO are localized on both the imino and isatan groups.

The chemical reactivity of the inhibitors that is resulting in adsorption on the metallic ion surface is a function of energy difference (ΔE) between the E_{HOMO} and E_{LUMO} of the inhibitor. Generally, higher reactivity between metallic ion and corrosion inhibitor is as a result of decrease in the value of ΔE and increases the binding ability on the surface of the metal which consequently increases in inhibition efficiency (%IE) of the inhibitor. However, the value of ΔE for the two molecules (Table 1) is the same: Molecule 1 ≈ Molecule 2, making this parameter difficult to further predict molecules of higher adsorption and enhanced inhibition efficiency. Further evaluation of the stability and reactivity of an inhibitor in order to predict the adsorption and inhibition efficiency of the studied molecules were determined using chemical hardness and softness which are quantum reactivity descriptors.

Table1. Quantum chemical reactivity descriptors of Molecule 1 and 2 estimated with DFT/B3LYP/6-31G(d)

Quantum descriptors	Molecule 1	Molecule 2
E_{HOMO} (eV)	-5.61	-5.59
E_{LUMO} (eV)	-3.01	-2.99
ΔE (eV)	2.6	2.6
η (eV)	1.3	1.3
S(eV^{-1})	0.77	0.77
ΔN	1.03	1.04
Log P	0.12	1.48
ovality	1.52	1.59
PSA	50.089	40.194
polarizability	66.79	74.68
$E_{solv\ (KJ/MOL)}$	-86.65	-73.62
IP	5.61	5.59
EA	3.01	2.99
χ	4.31	4.29
ω	7.14	7.08
V	320.89	418.14
aREA	345.11	428.65
DM (debye)	9.14	9.44
$\Delta E_{back\text{-}donation}$	-1.078	-1.072
MW (amu)	348.45	430.556
Energy	-47539.39	-53821.6

Note: s=softness, ω=global electrophilicity index, ΔE = energy difference, χ=electronegativity, η = hardness, ΔN=Electron transfer, V=Volume, M.W=Molecular Weight and DM= dipole moment

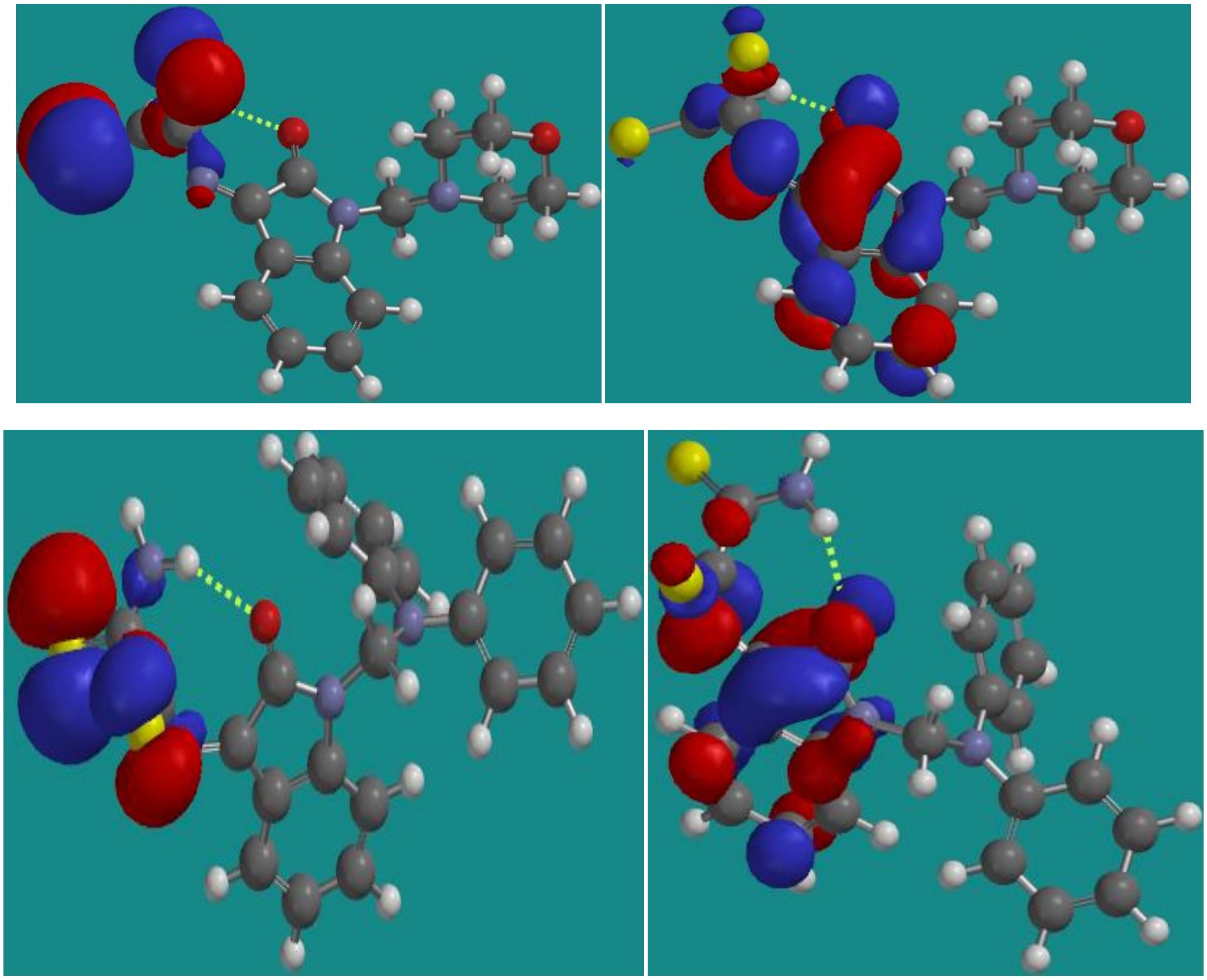

Figure 3. Optimized molecular structures of molecule 1 and 2 determined by DFT/B3LYP/6-31G*.

Hard molecules, atoms or ions will resist the deformation of electron clouds in an atom, molecules or ions with minor perturbations of the chemical reaction. The values of the absolute hardness 1.3 eV for both molecules 1 and 2 and softness 0.77 eV for both studied molecules are similar to the values obtained from energy different parameters. The softness followed the same trend of hardness: Molecule ≈ Molecule 2.
These results are expected since the ΔE for the two molecules are the same, and that the hardness and softness values are expected to be the same. The inhibition efficiency of these molecules using these parameters: ΔE, hardness and softness cannot be theoretically predicted. Although, better adsorption or enhanced inhibition efficiency can be predicted using the ability of an inhibitor to bind to the metallic surface as the E_{HOMO} increased and E_{LUMO} reduced (as the case of molecule 2), but these parameters are also not enough to ascertain their inhibition efficiency. Hence other parameters need consideration.

Electronegativity is another parameter that is associated with the tendency of an atom in a molecule to attract the shared pair of electrons to itself. The order of electronegativity values of studied molecules (Table 1) is as follows: Molecule 2 < Molecule 1. Also, the electronegativity difference between the inhibitor and the metal follows the order of Molecule 2 > Molecule 1. Following the Sanderson's principle of electronegativity equalization, Molecule 1 with a low electronegativity difference gets to equalization quickly and therefore low reactivity is expected, which, in turn, indicate that the molecule has low inhibition efficiency (Udhayakala *et al.*, 2012).

The Dipole Moment (DM) of inhibiting molecules predicts the direction of the corrosion inhibition process. It is defined as the product of the magnitude of the separated charge and the separation distance. It provides information on the bonds polarity and electron distribution in a molecule (Ebenso *et al*., 2010). The high value in dipole moment of inhibitors tends to increase their adsorption on the metallic surface to provide better inhibition. The deformability energy increases as the dipole moment dipole moment increases. This gives organic inhibitors easier adsorption to the metallic surface. The dipole moment of the studied molecules is observed in the following order: Molecule 2 > molecule 1. Therefore, it is expected that molecule 2 with dipole moments of 9.44 debye should adsorb easily on the surface of the metal than molecule 1 since adsorption of polar compounds with higher dipole moment enhances inhibition efficiency. The trend in polarizability of the studied molecules follows the order: Molecule 2 > Molecule 1 indicating that Molecule 2 might be having better inhibition efficiency.

The electrons transferred (ΔN) in a molecule predict the ability of a molecule to donate electrons to the metal surface. ΔN with higher value indicates greater tendency to donate electrons to the electron deficient site and consequently, greater tendency to interact and adsorb on the metallic surface. The ΔN values for molecules 1 and molecule 2 are 1.03 and 1.04 respectively. Organic molecules with lowest ΔN give the least inhibition efficiency (Udhayakala *et al*., 2012). This means that more transferred electrons (ΔN) is associated with molecule 2 which is a molecule with a better inhibition efficiency more than molecule 1. The ΔN results in Table 1 correlate with the experimentally determined inhibition efficiency of the studied compounds. It should also be noted that electrons can be transferred back to the inhibiting molecules from the metal through the process called electronic back donation. The Back donation charges -1.078 and -0.072 e^- from Table 1 shows that electronic back donation process can take place during the process of interaction between the studied molecules and metal ions since their values are less than zero. The charges transferred to the molecule are energetically favoured when η >0 and $\Delta E_{\text{back-donation}} < 0$. Therefore, Molecule 1 could be more energetically favoured to transfer electrons back to itself than Molecule 2. The result is consistent with the concept that states that if both charge transfer occurs (*i.e.* to the molecule and process of reverse donation processes from the molecule), the energy changes directly proportional to the hardness of the molecule.

Global electrophilicity index (ω) provides information on the nucleophilicity and electrophilicity nature of inhibiting molecules. Inhibitors with a high electrophilic index act as electrophile, while low electrophilicity act as nucleophile. The electrophilicity values (Table 1) of the studied molecule 1 is 7.14 and molecule 2 is 7.08 The log P which gives information about the hydrophobicity of organic molecules can be related to how effective iminoisatin derivatives will inhibit corrosion. Hydrophobicity increases when there is a decrease in the solubility. When studying corrosion, hydrophobicity can be associated with the formation of an oxide/hydroxide layer, which retards the corrosion process on the metal surface. The value of Log P for molecule 1 (0.12) and molecule 2 (1.48) confirmed that molecule 2 possesses higher inhibition efficiency than molecule 1. Weight and volume of the studied molecules which measure the molecular size and effectiveness of the molecular coverage on the metal surface were also considered. As these parameters increase in value, also, the corrosion inhibition potentials of the molecules increase (Quraishi *et al.,* 2010). The values of the weight and volume of molecule 2 is more than molecule 1. Thus molecule 2 is predicted to cover and adsorb more on the surface of a metal than molecule 1.

CONCLUSION

The molecular reactivity descriptors of studied molecules were probed in order to elucidate their electronic structures, reactivity and predict their efficiency toward corrosion inhibition using quantum mechanical method. The result obtained from DFT/B3LYP/6-31G(d) suggests a correlation between the studied quantum parameters and experimentally determined inhibition efficiency of iminoisatin derivatives. It was found that the correlations are useful in designing iminoisatin inhibitors with suitable substituents capable of donating electrons to the surface of the metal. Molecule 2 is theoretically confirmed to have the highest inhibition efficiency due to their higher E_{HOMO}, lower E_{LUMO} and ΔN values which would allow effective electron transfer and therefore better efficiency as a corrosion inhibitor.

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