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Quantum Chemical Study on the Corrosion Inhibition of Some Bipyrazoles.

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ABSTRACT

A theoretical study for three derivatives of bipyrazole namely ethyl 5,5'-dimethyl-1'*H*-1,3'-bipyrazole-4-carboxylate (Bip1) and 3-(bromomethyl)-5,5'-dimethyl-1'*H*-1,3'-bipyrazole (Bip3), which are recently used as corrosion inhibitors for steel in 1.0 M HCl medium, was undertaken by Density Functional Theory (DFT) at the B3LYP level. The calculated quantum chemical parameters correlated to the inhibition efficiency are The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), global softness (σ), ionization potential (I), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and the total energy (TE). The order of inhibition efficiency of the bipyrazole derivatives was found to be in agreement with experimental corrosion inhibition efficiencies.

Keywords: Corrosion inhibition, Bipyrazole, Density functional theory (DFT), softness indices.

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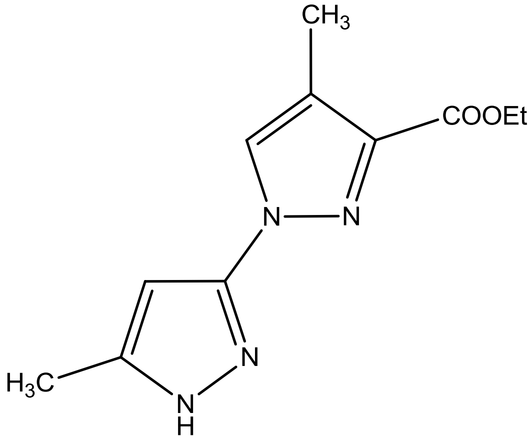
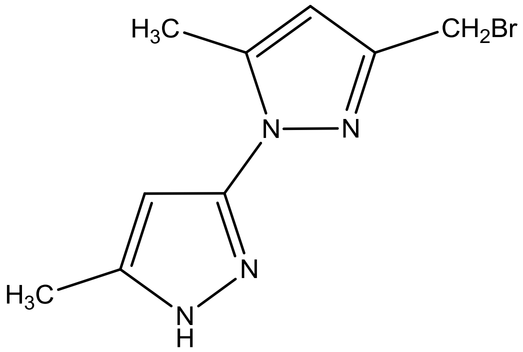
INTRODUCTION

Corrosion inhibitors are widely used in acid solutions for protection of metal surfaces from corrosion. Several organic compounds with hetero atoms like O, N, S, P and having multiple bonds are useful and are widely used as effective corrosion inhibitors [1-23]. In different acid solutions the corrosion inhibition of metals generally depends on how the metals are interacting with the concerned organic molecule [24]. The organic molecules should have centres which are capable of forming coordination bonds with metal surfaces [25,26]. Stronger is the coordination bond, better is the inhibition efficiency. Their effectiveness as promising inhibitors is related to spatial molecular structural distribution, molecular electronic structure, chemical composition, surface charge density and of course to their affinity to the individual metal surface [27-29].

In this present paper quantum chemical calculation have been performed to investigate the reaction mechanism of corrosion inhibition behaviour of bipyrazole and its derivatives. It strengthen the fact that this type of calculation are proving to be a very important and cost effective tool for corrosion inhibition mechanism even without doing each and every wet chemical studies [30,31]. In recent times, with the massive advancement of computational hardwares, DFT have emerged as an attractive tool to the scientific community for predicting structural behaviour and reaction mechanism of several chemical species. By using this sophisticated computational method we can easily predict the systematic way for the analysis of the inhibitor/surface interaction. The inhibitor properties of different bipyrazole derivatives have been reported in a recent experimental study. They proposed the inhibition efficiency increase in the order ethyl 5,5'-dimethyl-1'*H*-1,3'-bipyrazole-4-carboxylate (Bip1) < 3-(bromomethyl)-5,5'-dimethyl-1'*H*-1,3'-bipyrazole (Bip3) [15]. The molecular structures of the investigated bipyrazole derivatives are shown in Fig. 1.



ethyl 5,5'-dimethyl-1'*H*-1,3'-bipyrazole-4-carboxylate (Bip1).



3-(bromomethyl)-5,5'-dimethyl-1'*H*-1,3'-bipyrazole (Bip3).

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

The very aim of this particular work is to extend this investigation to ascertain whether the experimentally predicted orders are fully supported by theoretical predictions by finding a clear relationship between calculated quantum chemical parameters and the experimentally determined inhibition efficiency of inhibitors. This is achieved by calculating relevant molecular properties of inhibitors and there by explaining the mechanism of inhibition of the inhibitors with the steel surface. The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), global softness (σ), ionization potential (I), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and the total energy (TE).

QUANTUM CHEMICAL CALCULATIONS

Complete geometrical optimizations of the investigated molecules are performed using DFT (density functional theory) with the Beck's three parameter exchange functional along with the Lee-Yang-Parr nonlocal correlation functional (B3LYP) [32-34] with 6- 31G* basis set is implemented in Gaussian 03 program package [35]. This approach is shown to yield favorable geometries for a wide variety of systems. This basis set gives good geometry optimizations. The geometry structure was optimized under no constraint. The following quantum chemical parameters were calculated from the obtained optimized structure: The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), global softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN) and the total energy (TE).
According to Koopman's theorem [36], the ionization potential (E) and electron affinity (A) of the inhibitors are calculated using the following equations.

$$E = -E_{HOMO} \tag{1}$$

$$A = -E_{LUMO} \tag{2}$$

Thus, the values of the electronegativity (χ) and the chemical hardness (η) according to Pearson, operational and approximate definitions can be evaluated using the following relations [37]:

$$\chi = \frac{E+A}{2} \tag{3}$$

$$\eta = \frac{E-A}{2} \tag{4}$$

Global chemical softness (*σ*), which describes the capacity of an atom or group of atoms to receive electrons [38], was estimated by using the equation:

$$\sigma = \frac{1}{\eta} = -\frac{2}{E_{HOMO} - E_{LUMO}} \tag{5}$$

The number of transferred electrons (ΔN) was also calculated depending on the quantum chemical method [39, 40], by according the equation:

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

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of χ_{Fe} =7.0 eV and η_{Fe} = 0, for calculating the number of electron transferred.

RESULTS AND DISCUSSION

To determine a relationship between inhibitors and their corresponding inhibition efficiency, quantum chemical calculation are used herein. Optimised geometric structures and Mulliken spin density plots of HOMO and LUMO for the inhibitors were studied which supported the corrosion inhibition efficiency obtained from experimental results [13]. Calculations were performed with DFT using B3LYP function. The chemical structure of the molecules under investigation were presented in Table 1 and their optimised geometric structures, frontier molecular orbital densities are presented in Figures 2,3. Quantum chemical parameters, such as The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), global softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN) and the total energy (TE) are tabulated in Table 1.

The adsorption ability of the molecule over metal surface is related to their FMO (frontier molecular orbital) *i.e*; highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [41,42]. HOMO is associated with capability of a molecule to donate electrons whereas LUMO indicates its cability to accept electrons. From Figures 2,3, it can be seen that the electronic density in HOMO and LUMO on the entire area of each molecule are quite uniform which is due to its π-electron cloud density. The analysis of orbital HOMO and LUMO (Figures 2,3), we have shows that the preferential area of nucleophilic attack to the two molecules are the atoms of Bipyrazolique cycle.


Bip1 **Bip3**

Figure 2 : Optimized structure of Bip1 and Bip3.

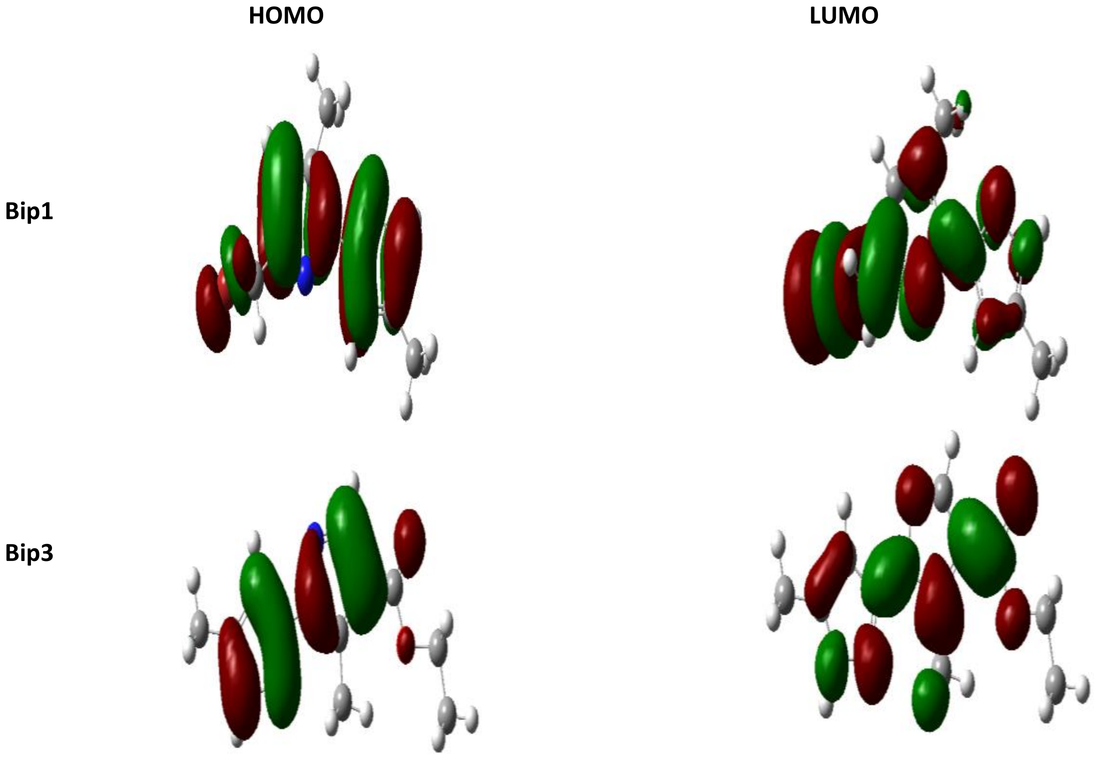


Figure 3: Molecular orbital of the studied Bipyrazoles showing the HOMO and the LUMO.

Table 1: Calculated quantum chemical parameters of the studied inhibitors.

Quantum parameters	Bip1	Bip3
E_{HOMO} (eV)	- 6.1136	-5.96037
E_{LUMO} (eV)	- 0.5593	-0.5075
ΔE gap (eV)	5.5543	5.4528
μ (debye)	5.5500	5.3501
$I = -E_{HOMO}$ (eV)	6.1136	5.96037
$A = -E_{LUMO}$ (eV)	0.5593	0.5075
$\chi = \frac{I+A}{2}$ (eV)	3.33645	3.23393
$\eta = \frac{I-A}{2}$ (eV)	2.77715	2.72643
$\sigma = \frac{1}{\eta}$	0.36008	0.36678
$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})}$	0.65958	0.69065
TE (eV)	-21679.672	-85415.375

Highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}) are very popular quantum chemical parameters. These orbitals, also called the frontier orbitals, determine the way the molecule interacts with other species. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants [43]. E_{HOMO} is often associated with the electron donating ability of the molecule. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital. Increasing values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer [44,45]. E_{LUMO} indicates the ability of the molecules to accept electrons. The lower values of the E_{LUMO}, the more probable it is that the molecule would accept electrons. A low value of the energy band gap ($\Delta E = E_{LUMO} - E_{HOMO}$) gives good inhibition efficiencies, because the energy to remove an electron from the last occupied orbital will be low [46].

From Table 1, it is evident that the E_{HOMO} for the inhibitors decreases in the order; (Bip3 > Bip1), which is consistent with the experimental % inhibition efficiency results. However, the E_{LUMO} decreases in a similar order. This can be explained as follows. The E_{LUMO} indicates the ability of the molecule to accept electrons. Therefore, the lower the value of E_{LUMO} the more apparent it is that the molecule would accept electrons. Also, the $E_{LUMO\text{-}HOMO}$ (energy gap) was also found to decrease in the order similar to that of the E_{LUMO}. Literature reveals that a larger value of the energy gap indicates low reactivity to a chemical species because the energy gap is related to the softness or hardness of a molecule. A soft molecule is more reactive than a hard molecule because a hard molecule has a larger energy gap [47,48].

The dipole moment (μ) is an index that can also be used for the prediction of the direction of a corrosion inhibition process. Dipole moment is the measure of polarity in a bond and is related to the distribution of electrons in a molecule [49]. Although literature is inconsistent on the use of 'μ' as a predictor for the direction of a corrosion inhibition reaction, it is generally agreed that the adsorption of polar compounds possessing high dipole moments on the metal surface should lead to better inhibition efficiency. Comparison of the results obtained from quantum chemical calculations with experimental inhibition efficiencies indicated that the % inhibition efficiencies of the inhibitors increase with decreasing value of the dipole moment.

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 Bip3 with low hardness value 2.72643 (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(σ), which is a local property, has a highest value [52]. Bip3 with the softness value of 0.36678 eV has the highest inhibition efficiency. The table 1 shows the order of electronegativity as Bip1 > Bip3. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order Bip3 > Bip1. According to Sanderson's electronegativity equalization principle [53], Bip1 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.

Table 1 show among other parameters the calculated fraction of electrons transferred, ΔN for all the sulfonamides studied. The calculation was carried out using Eq. (6) [39,40] by using the theoretical χ value of 7 eV/mol and η value of 0 eV/mol for iron. The values of ΔN showed inhibition effect resulting from electrons donation which agrees with Lukovits et al. 's study [40]. If $\Delta N < 3.6$ (as obtained in this study), the inhibition efficiency increased with the increasing electron-donating ability at the metal surface. In this study, the two bipyrazoles were the electron donors at varying degrees, and the carbon steel surface was the acceptor thereby binding the compounds to the carbon steel surface resulting in inhibition adsorption layer against corrosion. The higher the value of ΔN, the higher the %IE and hence the better the compound as inhibitor. The order is as follows: Bip3 > Bip1 (like the order of %IE) for the neutral molecules. This shows that as the strength of the iron-inhibitor bond increased, the degree of corrosion inhibition also increased. Similar observation was also reported by Isaa et al. [54].

The total energy of molecule, including all forms of kinetic motion (translation, vibration, and rotation) and all forms of potential energy (electrostatic interaction between changes, magnetic interactions between spinning charges, and potential energy of bonds), determines the reactivity and stability of a molecule. It includes the energy in all the chemical bonds, and the energy of the free, conduction electrons in metals. The total energy has been calculated and correlated with experimental results. A satisfactory agreement is found between theoretical and experimental data. The higher the total energy (E_T), confirms the higher stability of the molecule and hence the lesser the tendency of it to the donating ability. From the results, it is evident that based on the decreasing values of the total energy (E_T), the trend for the variation of the inhibition efficiency follows the order: Bip3 > Bip1 with values-21679.672 eV > -85415.375 eV.

CONCLUSION

Quantum chemical parameters such as E_{HOMO}, E_{LUMO}, energy gap (ΔE), hardness (η), Softness (σ), electron affinity (A), ionization potential (E), the absolute electronegativity (χ), the fraction of electron transferred (ΔN) and the total energy (TE) were calculated using density functional theory at B3LYP/6-31-G* basis set. The inhibition efficiency of two substituted Bipyrazoles namely, ethyl 5,5'-dimethyl-1'*H*-1,3'-bipyrazole-4-carboxylate (Bip1) and 3-(bromomethyl)-5,5'-dimethyl-1'*H*-1,3'-bipyrazole (Bip3) has been investigated by utilizing quantum chemical approaches using the Density Functional Theory method. The inhibition efficiency of Bip1 and Bip3 increase with the increase in E_{HOMO}, and decrease in E_{LUMO}. BIP3 has the highest inhibition efficiency because it had the highest HOMO energy and ΔN values and it was most capable of offering electrons. The parameters like hardness(η), Softness(σ), and the fraction of electron transferred (ΔN) confirm the inhibition efficiency in the order of Bip3 >Bip1.

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