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DFT computational study of pyridazine derivatives as corrosion inhibitors for mild steel in acidic media

Robert Oluwaseyi Ogede*, Nurudeen Abdulafeez Abdulrahman and Dasola Airat Apata

Department of Science Technology, Federal Polytechnic, Ado-Ekiti, Nigeria.

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Abstract

The molecular structures of two Pyridazine derivative; 5-phenyl-6-ethyl-pyridazine-3-thione (PEPT) and 5-phenyl-6-ethylpyridazine-3-one (PEPO) were simulated for corrosion inhibition efficiency using quantum chemical calculations based on density functional theory (DFT) at the B3LYP/6-31G* basis set level in order to compare the relationship between their molecular structure, electronic structure and inhibition potential. The quantum chemical properties for inhibition efficiency such as EHOMO (energy of the highest occupied molecular orbital), ELUMO (energy of the lowest unoccupied molecular orbital), energy gap (ΔE), dipole moment (μ), global hardness (η), global softness (S), electronegativity (χ), electrophilicity (ω), nucleophilicity (ϵ), electrons transferred from inhibitors to metal surface (ΔN), and the energy change during electronic back-donation process (ΔE^*) were calculated. The results show that 5-phenyl-6-ethyl-pyridazine-3-thione (PEPT) would have higher inhibition efficiency than 5-phenyl-6-ethylpyridazine-3-one (PEPO) due to its relative EHOMO, ELUMO, ΔE , μ , η , S , χ , ω , ΔN , and ΔE^* .

Keywords: Inhibition Efficiency; DFT; Pyridazine Derivative; LUMO and HOMO

1. Introduction

Corrosion inhibition is substances added into any corroding environment with the intention of decreasing the corrosion rate of the metal. Therefore, a corrosion inhibitor may loosely be regarded as that substance which when added intentionally to an aggressive medium, decreases its rate of attack on a metal. Inhibitors are generally used to protect materials from deterioration due to corrosion [1]. Most of the well-known inhibitors used in industries are organic compounds having multiple bonds or containing N, S, O or P through which they get adsorbed onto the metal surface by means of their non-bonding electrons [2]. They possess π conjugate double bond and aromatic systems. This unique molecular structure makes it easy for them to be absorbed on the metal surface and block the active site thereby reducing corrosion.

Computational chemistry has made quantum chemical methods a more viable tool in determining the molecular structures, electronic structure, reactivity of molecules and to predict the corrosion inhibition performances of molecules because of the high cost of experimental methods and also because the study of the inhibition mechanisms of chemical compounds is time consuming [3]. Quantum chemical calculations have been widely used to studying corrosion inhibition mechanism [4-5]. Density functional theory (DFT) has provided a powerful framework for developing new criteria for rationalizing, predicting a theoretical chemical parameters such as (EHOMO), (ELUMO), the energy gap (ΔE), dipole moment (μ), ionization potential (I), electron affinity (A), electronegativity (χ), global hardness

* Corresponding author: Robert Oluwaseyi Ogede
Department of Science Technology, Federal Polytechnic, Ado-Ekiti, Nigeria.

(η), softness (S), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and back donation (ΔE^*) [6]. The local reactivity has been analyzed by means of the Fukui indices [7].

Pyridazine are diazine, which contain Nitrogen atoms in 1-2 relationship. Pyridazine compound are commonly used as anticancer, antituberculous, antihypertensive [8] antifungal [9] or antimicrobial [10] agents due to their intense biological activity. Pyridazine derivatives have also been studied as corrosion inhibitors, on various metals and in various environments, due to π electrons and nitrogen atoms in their ring [11]. Infact, some new synthesized Pyridazine derivatives were used in many research fields due to their structure, stability, reactivity and their tendency to form stable yields with important biological properties [12]. The influence of nitrogen-containing organic compounds, such as amines and heterocyclic compounds, on the corrosion of steel in acidic solution has been investigated by several workers [13] An investigation of two novel pyridazine derivatives as corrosion inhibitor for C38 Steel in 1.0 M HCl was reported by A. Ghazoui et al. [14]. In all acidic media, better performances are seen in the case of 5-benyl-6-methyl-pyridazine-3-thione (BMPT) and 6-phenylpyridazine-3(2H)-thione (PPT) [15, 16]. In this work, we will investigate the corrosion inhibition property of new Pyridazine derivatives using Density Function Theory method to calculate molecular descriptors of the factors responsible for the corrosion inhibitory properties of the studied compounds. In addition, we will correlate the calculated parameters to the reactivity and selectivity performances of the molecules as to observed inhibition efficiency.

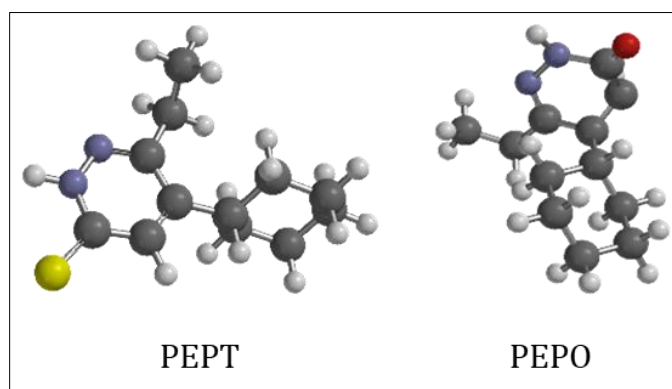


Figure 1 Optimized structure of 5-phenyl-6-ethyl-pyridazine-3-thione (PEPT) and 5-phenyl-6-ethylpyridazine-3-one (PEPO)

2. Computational Method and Model

All the computations were performed with Spartan 20 programs by wave function Inc. Density functional theory (DFT) method is a popular quantum mechanical calculation tool for probe into structures, reactivity and selectivity of chemical molecules [17]. DFT calculation was carried out on new Pyridazine Derivatives structure and optimized with the Becke's three parameter exchange functional along with the Lee- Yang-Parr non local correlation functional (B3LYP) and 6-31G* basis set in vacuum [18,19]. The molecular properties of the descriptors estimated include HOMO-LUMO energy gap (ΔE), total energy, dipole moment (μ), electronegativity (χ), hardness (η), softness (S), electrophilicity index (ω) and local reactivity Fukui function, $F(r)$ and local softness, $s(r)$ using the following equation [20,21].

Ionization potential (I) and 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 according to Koopman's theorem [22]

Ionization potential (I) is defined as the amount of energy required to remove an electron from a molecule [23]. It is related to the energy of the EHOMO through the equation:

$$I = EHOMO \dots \dots (1)$$

Electron affinity (A) is defined as the energy released when a proton is added to a system [23]. It is related to ELUMO through the equation:

$$I = EHOMO \dots\dots (2)$$

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

The electronegativity is the measure of the power of an atom or group of atoms to attract electrons towards itself [40], it can be estimated by using the equation:

$$\chi = \frac{I + A}{2} = -\frac{(EHOMO + ELUMO)}{2} \quad (3)$$

Chemical hardness (η) measures the resistance of an atom to a charge transfer [24], it is estimated by using the equation:

$$\eta = \frac{EHOMO - ELUMO}{2} = \frac{(I - A)}{2} \quad (4)$$

Chemical softness (S) is the measure of the capacity of an atom or group of atoms to receive electrons [25], it is estimated by using the equation:

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

The electrophilicity index

$$(\omega) = \frac{\mu^2}{2\eta} \quad (6)$$

Nucleophilicity (ε), which is the inverse of the electrophilicity is expressed as: [26]

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

When there is a close contact between an iron and an inhibitor, electrons flow from lower electronegative (inhibitor) to higher electronegative (iron), until their chemical potentials (μ) or electronegativities (χ) become equal. The fraction of electrons transferred (ΔN) is given as:

$$\Delta N = \frac{\chi^{Fe} - \chi^{Inh}}{2(\eta^{Fe} + \eta^{Inh})} \quad (8)$$

Where χ^{Fe} and χ^{Inh} represent the electronegativities of Fe (metal) and inhibitor respectively. η^{Fe} and η^{Inh} are the chemical hardness values of Fe (metal) and inhibitor respectively. In this study, the theoretical value of χ^{Fe} and η^{Fe} used to calculate the number of transferred electrons are 7 eV/mole and 0 eV/mole respectively [26].

The basic relationship of the density functional theory of chemical reactivity is precisely, the one established by Parr et al., [21], 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.

$$\mu = -\chi = \left(\frac{dE}{dN}\right)_{v(r)} \quad (9)$$

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 [20].

$$\eta = \partial^2 E / \partial N^2 \eta = \left(\frac{d^2 E}{dN^2}\right)_{v(r)} \quad (10)$$

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

3. Results and Discussion

3.1. Effects of HOMO-LUMO energy gap

The study of energies of pairs of frontier orbitals, namely HOMO and LUMO of molecules provide reliable and quantitative data for straightforward prediction and comparative study of chemical and thermodynamic stabilities of molecules. EHOMO measure the ability of a molecule to donate electron and ELUMO measure the ability of a molecule to accept electron. It has been shown that molecules with high value of EHOMO indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on mild steel and therefore better inhibition efficiency. Similarly a low value of ELUMO will be required for higher inhibition efficiency [27]. From table 1, PEPT with higher EHOMO (-5.53eV) value and lowest ELUMO (-1.87eV) value has the highest inhibition efficiency, and PEPO with the lowest EHOMO (-6.03eV) value and the highest ELUMO (-2.13eV) value has the least inhibition efficiency. The binding ability of the inhibitor to the metal surface increases with increasing of the HOMO and decreasing of the LUMO energy values. The highest value of EHOMO and ELUMO of PEPT indicates the better inhibition efficiency than PEPO

HOMO-LUMO energy gap (ΔE) is an important stability index [28]. and gives information about 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. A lower value of energy gap signifies higher reactivity of the inhibitor, which will translate to a higher binding ability of the inhibitor on the surface of the metal [29]. A large energy gap implies higher stability and lower chemical reactivity of inhibitor and vice versa. From the calculations made (table 1) using DFT at the B3LYP/6-31G* basis set level, PEPT has the lowest energy gap and could act as a better corrosion inhibitor. Figure 2 and 3; show the HOMO and LUMO of the studied molecules

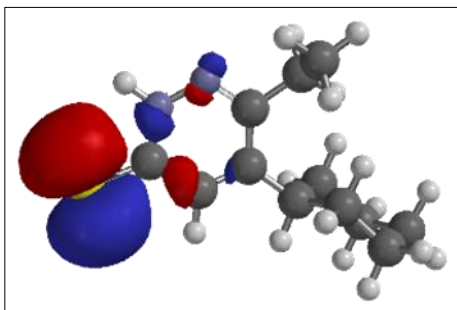


Figure 2 (a) The highest occupied molecular orbital (HOMO) density of PEPT using DFT at the B3LYP/6-31G* basis set level

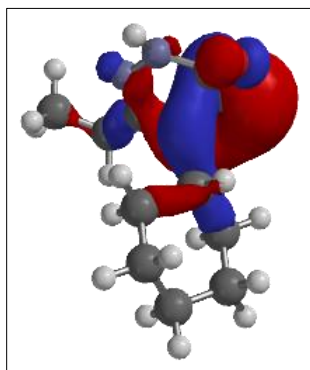


Figure 2 (b) The highest occupied molecular orbital (HOMO) density of PEPO using DFT at the B3LYP/6-31G* basis set level

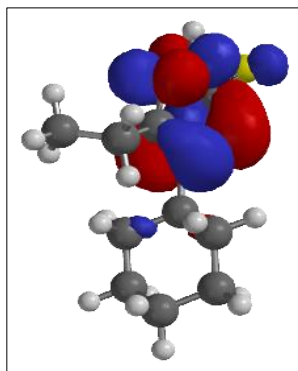


Figure 3 (a) The Lowest unoccupied molecular orbital (LUMO) density of PEPT using DFT at the B3LYP/6-31G*basis set level

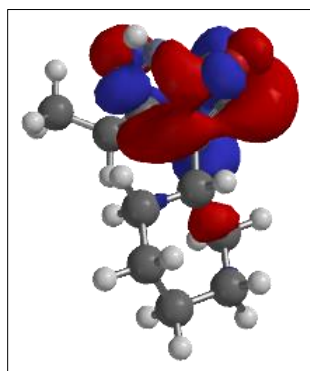


Figure 3 (b) The Lowest unoccupied molecular orbital (LUMO) density of PEPO using DFT at the B3LYP/6-31G*basis set level

3.2. Dipole moment

Another parameter that helps in the understanding of interaction between atoms in the same or different molecules is the dipole moment. It is a measure of the net molecular polarity, which is the magnitude of charge ($/Q/$) at the either ends of the molecular dipole time the distance between the charges. Dipole moment increases with increase in electronegativity of atoms [30]. Chemical reactivity usually increases with increase in dipole moment. The high value of dipole moment probably increases the adsorption between chemical compound and metal surface [31]. The volume of the inhibitor molecules also increases with the increase of dipole moment. This increases the contact area between the molecule and surface of iron and increasing the corrosion inhibition ability of inhibitors. In our research, the value ($\mu = 6.61$ Debye) of PEPT suggest its better inhibition efficiency.

3.3. Total Energy

The total energy calculated by quantum mechanical method is also a beneficial parameter. The total energy determines the occurrence or non-occurrence of chemical reactions and stereospecific paths in intra- and inter-molecular processes [32]. The total energy of a system is composed of the internal, potential, and kinetic energy. Hohenberg and Kohn [33] proved that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy. From our study, the total energy (absolute values) of PEPO is higher than that of PEPT.

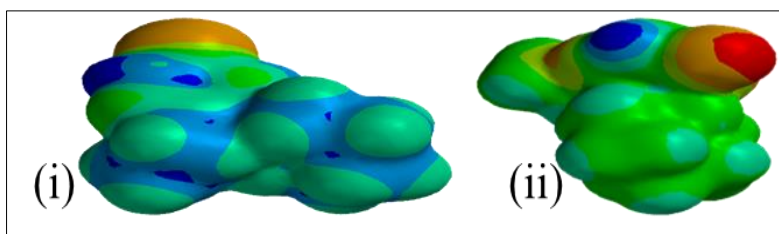


Figure 2 The local ionization potential of (i) PEPT and (ii) PEPO

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

PARAMETERS	PEPT	PEPO
HOMO(eV)	-5.53	-6.03
LUMO(eV)	-1.87	-2.13
Energy gap(ΔE)eV	3.66	3.90
Dipole moment (μ)debye	6.16	3.32
Total Energy (E)au	-975,805850	-652.718566

3.4. Global hardness and Global softness

Global hardness and global softness According to the HSAB principle of Pearson, [34], within the framework of density functional theory, chemical reactivity and stability of a molecule is associated with its global hardness (η) and global softness (s) calculated using equation 4 and 5. Increase in hardness increases movement of the system towards a more stable configuration-equilibrium configuration. When a molecule moves away from its equilibrium configuration, its hardness value decreases. Greater hardness therefore implies high stability and low reactivity. Global softness has an inverse relationship with hardness: soft molecules undergo changes in electron density more easily than the hard molecules and are more reactive than the hard molecules [35]. A hard molecule has a large energy gap and a soft molecule has a small energy gap. Hence very efficient inhibitors are expected to have lower value of chemical hardness and greater value of softness [36] In this study, PEPT have the lowest value of global hardness (1.83eV) and with low energy gap (3.66eV) compared with PEPO with highest value of global hardness and large energy gap of 1.95eV and 3.90eV respectively. Normally, the inhibitor with the least value of global hardness and the highest value of global softness is expected to have the highest inhibition efficiency [37]. PEPT with the softness value of 0.55eV has the highest inhibition efficiency.

Table 2 Molecular Descriptors Obtained for the pyridazine Derivative calculated using B3LYP/6-31G (d,p)

PARAMETERS	PEPT	PEPO
Global hardness (η)(eV)	1.83	1.95
Global softness(s)(eV)	0.55	0.51
Electronegativity (χ)	3.88	4.08
Electrophilicity index(ω)	10.37	2.83
Nucleophilicity(ϵ)	1.82	1.96
Ionization potential (IE %)	5.53	6.03

Electronegativity (χ) in table 1, PEPT < PEPO. According to Sanderson's electronegativity equalization principle [38]. PEPO with a high electronegativity and low difference of electronegativity quickly reaches equalization and low reactivity is expected which in turn indicates low inhibition efficiency.

Electrophilicity index (ω) means the tendency of a molecule to receive electrons, while nucleophilicity (ϵ) means the tendency to donate electrons to others. A molecule with a large electrophilicity value will not be an efficient corrosion inhibitor while a molecule that has a large nucleophilicity value is expected to be an excellent corrosion inhibitor [39]. In our study, as shown in table 2, PEPT have the highest electrophilicity index and low nucleophilicity compared to PEPO, has the highest inhibition efficiency.

Ionization energy is also within the framework of density functional theory, chemical reactivity and stability of atoms and molecules. Fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and low chemical reactivity. While, small ionization energy indicates high chemical reactivity of the atoms and molecules [40]. The low ionization energy 5.53eV of PEPT indicates the high inhibition efficiency

Table 3 The number of electron transferred (ΔN) and ΔE^* back-donation calculated for inhibitor PEPT and PEPO

Parameters	PEPT	PEPO
Electron transferred fraction (ΔN)eV	0.85	0.75
Back-donation (ΔE^*)	-0.46	-0.49

The electron transferred (ΔN) is the propensity of a molecule to donate electrons and the greater the value of ΔN , the greater the propensity of a molecule to donate electrons to the electron poor species. Table 2, show the number of electrons transferred (ΔN) and back-donation (ΔE^*) calculated. According to Lukovits et al., (2001) if $\Delta N < 3.6$, the inhibition efficiency increased with increasing electron donating ability at the metal surface. It was also describe that the positive number of electrons transferred (ΔN) point out that the molecules act as an electron acceptor, while a negative number of electrons transferred (ΔN) indicates that the molecules act as electron donors. In this case of the molecules studied, values of ΔN are < 3.6 eV and are all positive, suggesting that all the studied molecules are good electron acceptors, resulting in good inhibition efficiency. Thus, the highest fraction of electrons transferred is associated with the best inhibitor (PEPT), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (PEPO).

It is important to consider a simple charge transfer theory for donation and back-donation of charges. When the electron transfer and back-donation processes occur at the same time, the energy change is directly proportional to the hardness of the inhibitor molecule [42]. This means that when $\eta > 0$, and $\Delta E^* < 0$, back-donation from the molecule to the metal is energetically favored. Based on this, it is evident that ΔE^* will increase while hardness decreases. As shown in Table 2 and 3, the calculated ΔE^* increases as the %IE increases.

4. Conclusion

On the basis of this study, the two pyridazine derivatives: 5-phenyl-6-ethyl-pyridazine-3-thione (PEPT) and 5-phenyl-6-ethylpyridazine-3-one (PEPO) investigated by utilizing DFT quantum chemical approaches for inhibition efficiency. The results showed that 5-phenyl-6-ethyl-pyridazine-3-thione (PEPT) will be more effective in terms of the prevention of corrosion of mild steel in acidic solution judged from the values of their EHOMO, ELUMO, energy gap (ΔE), dipole moment (μ), global hardness (η), global softness (S), electronegativity (χ), electrophilicity (ω), nucleophilicity (ϵ), electrons transferred from inhibitors to metal surface (ΔN), and the energy change during electronic back-donation process (ΔE^*) calculated, However, experimental verification would be needed to further ascertain adherence to these predictions.

Compliance with ethical standards

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Disclosure of conflict of interest

The Authors declare that there is no conflict of interests regarding the paper production.

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