Theoretical assessment of corrosion inhibition performance of some pyridazine derivatives on mild steel

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ABSTRACT

The inhibition potentials of two pyridazine derivatives 5-benzyl-6-methyl pyridazine-3-thione (BMPT) and 5-benzyl-6-methyl pyridazine-3-one(BMPO) has been elucidated using quantum chemical calculations based on density functional theory (DFT) at the B3LYP/6-31G(d,P) basis set level in order to investigate the relationship between their molecular and electronic structure and inhibition efficiency. The quantum chemical properties such as E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap (ΔE), dipole moment (μ), hardness (η), softness (S), the absolute electronegativity (χ), the fractions of electrons transferred (ΔN) and the electrophilicity index (ω) were calculated. The local reactivity has been analyzed through the Fukui function and condensed softness indices in order to compare the possible sites for nucleophilic and electrophilic attacks. The obtained theoretical data agree well with the experimental results.

Keywords: Pyridazine, corrosion inhibition, DFT, Fukui function, electrophilicity index.

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INTRODUCTION

Corrosion of mild steel is an inevitable process that has attracted many investigation and researches [1]. The study of corrosion process and their inhibition by organic inhibitors is a very active field of research [2]. A number of heterocyclic compounds containing N, O, and S either in the aromatic or long chain carbon system have been reported as effective inhibitors of metal corrosion [3,4]. The inhibition mechanism is generally explained by the formation of a physically and / or chemically adsorbed film on the metal surface [5]. Most efficient inhibitors are organic compounds containing electronegative functional groups and π-electrons in triple or conjugated double bonds. 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, π orbital character and the molecular size [6,7].The inhibition efficiency has been closely related to the inhibitor adsorption abilities and the molecular properties for different kinds of organic compounds [8,9]. The power of the inhibition depends on the molecular structure of the inhibitor. Organic compounds, which can donate electrons to unoccupied d orbital of 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 [10].

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Quantum chemical calculations have been widely used to study reaction mechanism. They have been proved to be a very powerful tool for studying corrosion inhibition mechanism [11-13]. Density functional theory (DFT) [14,15] has provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes [16-18]. A variety of chemical concepts which are now widely used as descriptors of chemical reactivity, e.g., electronegativity [17] hardness or softness quantities etc., appear naturally within DFT [14]. The Fukui function [18] representing the relative local softness of the electron, measures the local electron density/population displacements corresponding to the inflow of a single electron. They have been successfully performed to link the corrosion inhibition efficiency with molecular orbital (MO) energy levels for some kinds of organic compounds [19, 20].

The pyridazine and their derivatives are reported to exhibit a broad range of biological activity, such as analgesic [21], antibacterial [22], anti-inflammatory [23], antihypertensive properties [24]. They have attracted considerable attention in the recent years for their diverse anti diabetic [25] and also as human rhinovirus (HRV-3) inhibitors[26]. *L.M.C. Vieira et al.,* have studied the electrochemical and spectroscopic studies of some Pyridazine derivatives[27]. *A. Zarrouk et al.,* have investigated the comparative study of new Pyridazine derivatives towards corrosion of copper in nitric Acid [28]. 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.*[29].

Although experimental work of *A. Chetouani et al.* [30] provide valuable information on the corrosion inhibition efficiency of two pyridazine derivatives 5-benzyl-6-methyl pyridazine-3-thione (BMPT) and 5-benzyl-6-methyl pyridazine-3-one(BMPO), a deep understanding of the inhibition property remain unclear. The objective of the present paper is to extend the study of *A.Chetouani et al.* [30] by analyzing the inhibition efficiency of BMPT and BMPO on theoretical chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (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). 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.

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EXPERIMENTAL SECTION

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2.1 Quantum Chemical Calculation

In order to explore the theoretical-experimental consistency, quantum chemical calculations were performed using Gaussian-03 software package [31]. 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) [32,33]. 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 [34]. Recently, Density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/ surface mechanism and to describe the structural nature of the inhibitor in the corrosion process [35]. The chemical and optimized structures of the compounds studied are given in Fig 1. and Fig 2.

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5-benzyl-6-methyl pyridazine-3-thione
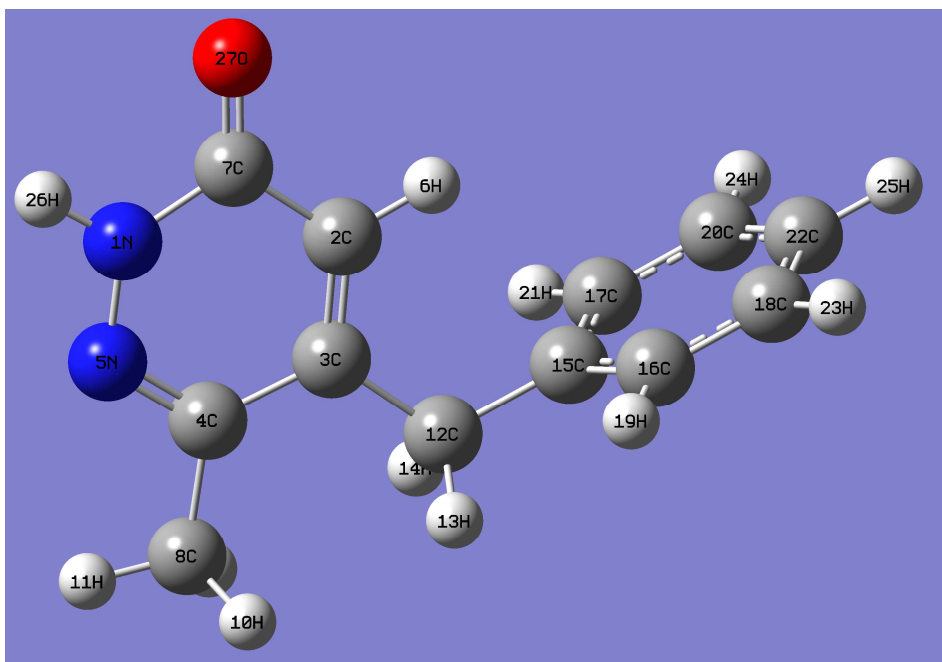(BMPT)

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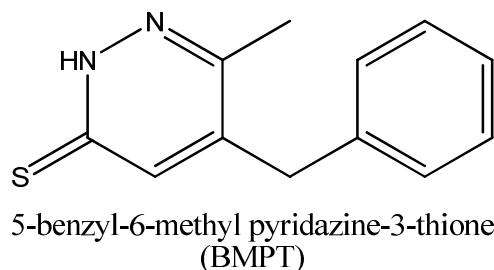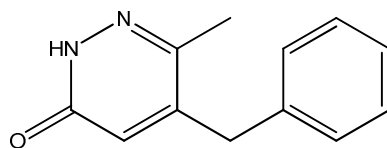
5-benzyl-6-methyl pyridazine-3-one
(BMPO)

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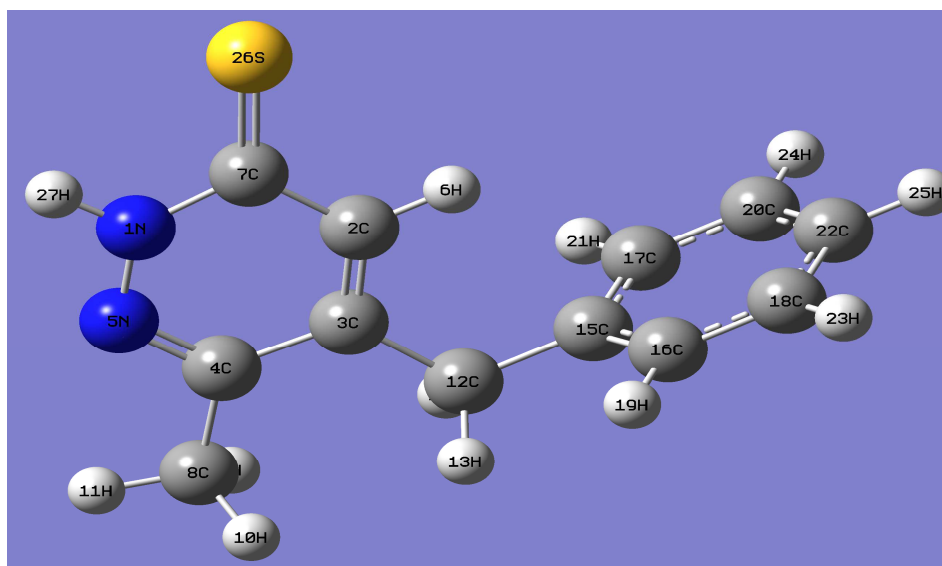
BMPT

BMPO

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

144

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2.2. Theoretical background
Global quantities

Density functional theory (DFT) [14] 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 (χ), hardness (η), softness(S), electrophilicity index(ω) 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 et al.,* [36], 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.

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

Where μ 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 (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 [37].

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

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

According to Koopman's theorem [38], 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.

Ionization potential (I) is defined as the amount of energy required to remove an electron from a molecule [39]. It is related to the energy of the E_{HOMO} through the equation:

I = -E_{HOMO} (3)

Electron affinity (A) is defined as the energy released when a proton is added to a system [39]. 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 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:

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

Chemical hardness (η) measures the resistance of an atom to a charge transfer [41], it is estimated by using the equation:

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

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Chemical softness (S) is the measure of the capacity of an atom or group of atoms to receive electrons [41], 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 potentials are equal [42]. Therefore the fraction of electrons transferred (*ΔN*) from the inhibitor molecule to the metallic atom was calculated according to Pearson electronegativity scale [43]

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

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule respectively 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 [44] and η_{Fe} = 0 by assuming that for a metallic bulk I = A [45] 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* [46] have proposed electrophilicity index as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index(ω) 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 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.

2.3. Local molecular reactivity

Fukui functions were computed since it provides an avenue for analyzing the local selectivity of a corrosion inhibitor [47]. 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 [48].

$$f_k^+ = q_{N+1} - q_N \tag{10}$$

$$f_k^- = q_N - q_{N-1} \tag{11}$$

where q_N, 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 $s(r)$ [49]

$$s(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)} \left(\frac{\partial N}{\partial \mu} \right)_{v(r)} = f(r)S \tag{12}$$

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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*., [50] 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.

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

The $\Delta E_{Back\text{-}donation}$ implies that when $\eta > 0$ and $\Delta E_{Back\text{-}donation} < 0$ 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 [51]. 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. 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 BMPT and BMPO is represented in fig. 3.

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

Parameters	BMPT	BMPO
E_{HOMO}(eV)	-5.52676	-6.21821
E_{LUMO} (eV)	-1.81177	-1.39815
Energy gap(ΔE) (eV)	3.71506	4.82006
Dipole moment (Debye)	5.6775	4.0670

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[52]. 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} -5.52676 (eV) of BMPT indicates the better inhibition efficiency than the other compound.

The energy of the lowest unoccupied molecular orbital, E_{LUMO}, indicates the ability of the molecule to accept electrons [36]. So, the lower the value of E_{LUMO}, the more probable the molecule to accept electrons. In our study the BMPT having low value of E_{LUMO} could have better performance as corrosion inhibitor.

The 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 [53]. Hard molecules have high HOMO-LUMO gap [54] and thus soft bases inhibitors are the most effective for metals [55]. The results as indicated in table 1 show that inhibitor BMPT has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor.

The dipole moment (μ in Debye) is another important electronic parameter that results from non uniform distribution of charges on the various atoms in the molecule. The high value of dipole moment probably increases

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the adsorption between chemical compound and metal surface [56]. The energy of the deformability increases with the increase in μ, making the molecule easier to adsorb at the Fe surface. The volume of the inhibitor molecules also increases with the increase of μ. This increases the contact area between the molecule and surface of iron and increasing the corrosion inhibition ability of inhibitors. In our study the value 5.6775 (Debye) of BMPT enumerates its better inhibition efficiency.

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 [57]. The low ionization energy 5.52676 (eV) of BMPT indicates the high inhibition efficiency.

Hardness and softness are the basic chemical concepts, called global reactivity descriptors has been theoretically justified within the framework of density functional theory(DFT) [14].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 [58]. In our present study BMPT with low hardness value 1.85749 (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 [59]. 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 [60]. BMPT with the softness value of 0.53836 has the highest inhibition efficiency.

The table 2 shows the order of electronegativity as BMPO > BMPT. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order BMPT > BMPO. According to Sanderson's electronegativity equalization principle [61],   BMPO 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.

Global electrophilicity index (ω) is the measure of the electrophilic tendency of a molecule. In our case, the inhibitor BMPT with high electrophilicity index value than the other compound, has the highest inhibition efficiency.

Table 2. Quantum chemical parameters for BMPT and BMPO calculated using B3LYP/ 6-31G(d,p).

Parameters	BMPT	BMPO
IE(eV)	5.52676	6.21821
EA(eV)	1.81177	1.39815
η (eV)	1.85749	2.41003
S (eV)	0.53836	0.41493
χ (eV)	3.66926	3.80818
ω	3.6241	3.0087
μ	-3.33926	-3.80818

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's study [62]. 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: BMPO < BMPT. 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 (BMPT), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (BMPO).

Table 3. The number of electron transferred (ΔN) and ΔE back donation (eV) calculated for inhibitor BMPT and BMPO .

| Parameters	BMPT	BMPO
Transferred electrons fraction (ΔN)	0.89657	0.66219
ΔE *b*ack-donation / (eV)	-0.46437	-0.6025

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 [63]. 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

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donate a certain amount of charge through the same centre or another one [50]. Parr and Yang proposed that larger value of Fukui function indicate more reactivity [18]. Hence greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule.

3.1 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.

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 molecules BMPT and BMPO are presented in Tables 4 and 5.
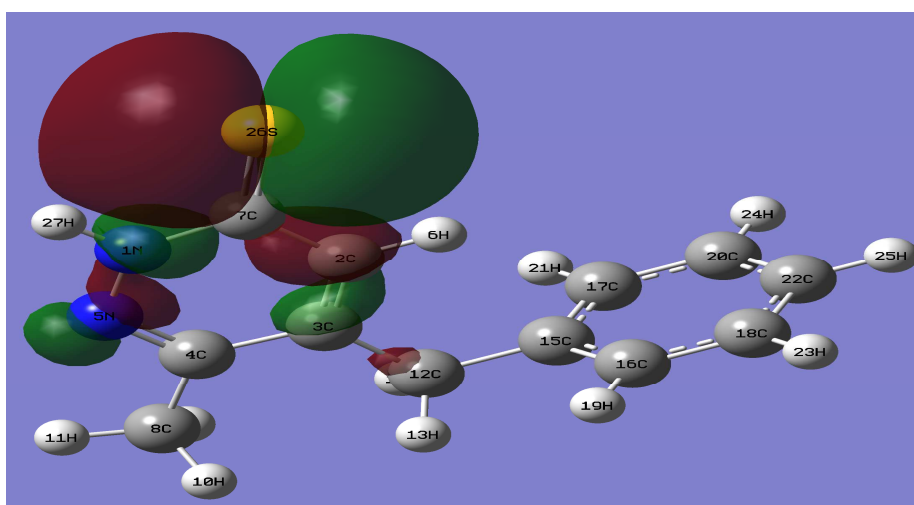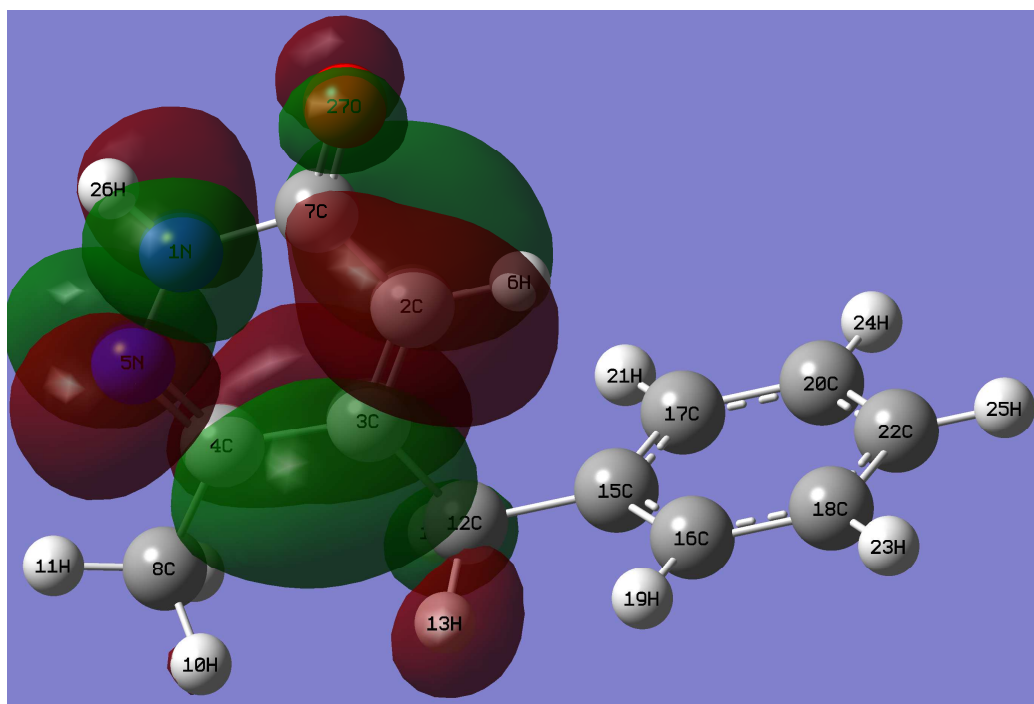

HOMO of BMPT
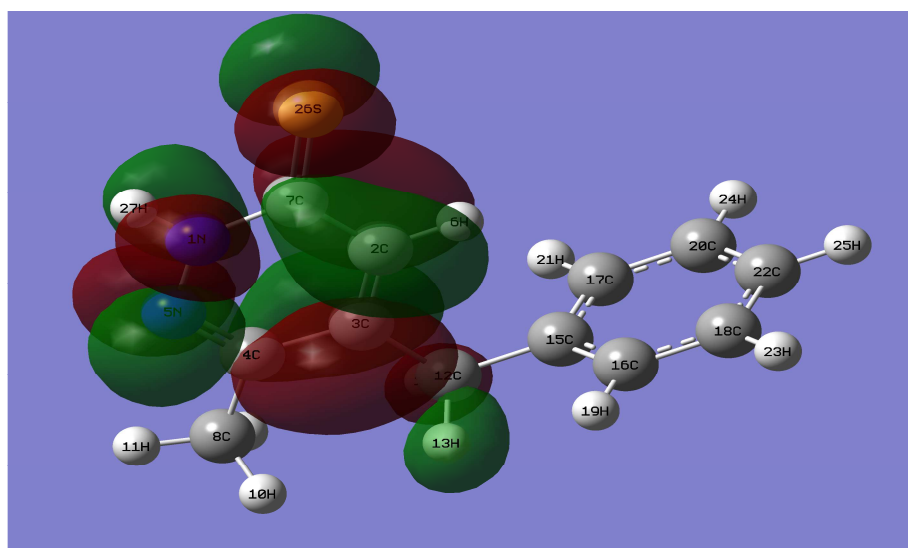
LUMO of BMPT
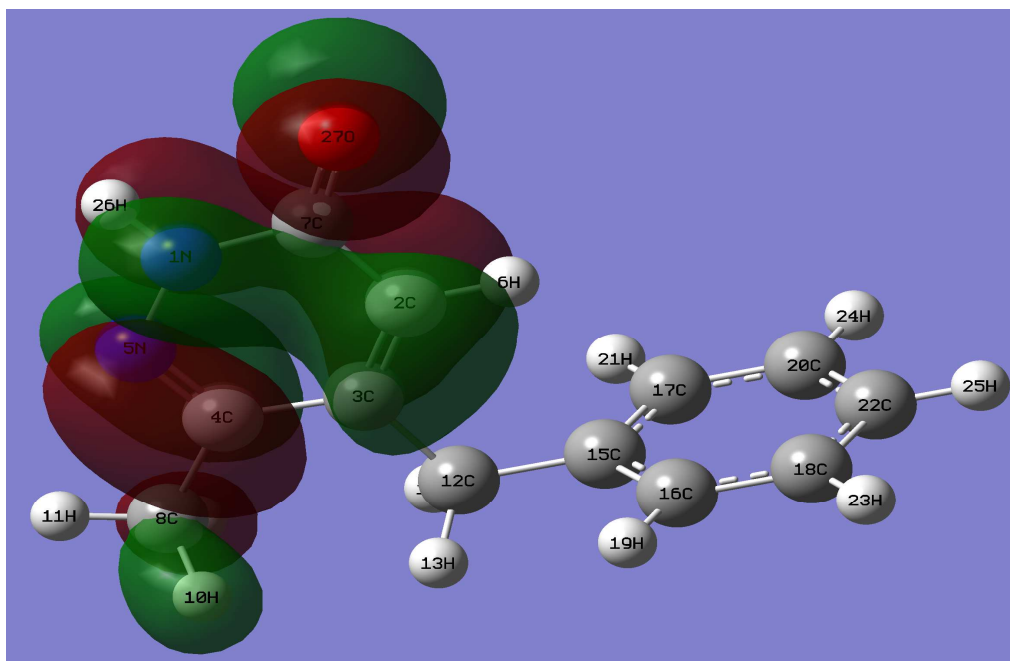
HOMO of BMPO

LUMO of BMPO

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

150

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

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 N	0.048153	0.065312	0.019980	0.027099
2 C	0.066988	0.053859	0.027795	0.022348
3 C	0.060183	0.016401	0.024972	0.006805
4 C	0.004431	0.01803	0.001838	0.007481
5 N	0.111762	0.058821	0.046373	0.024406
6 H	0.09568	0.050852	0.039701	0.0211
7 C	-0.025324	-0.073599	-0.010508	-0.030538
8 C	0.002633	-0.010883	0.001092	-0.004516
9 H	0.043512	0.042687	0.018054	0.017712
10 H	0.026728	0.043394	0.011090	0.018005
11 H	0.042206	0.038463	0.017512	0.015959
12 C	-0.008987	-0.012871	-0.003729	-0.005341
13 H	0.055384	0.03705	0.022980	0.015373
14 H	0.034895	0.039955	0.014479	0.016578
15 C	-0.050839	-0.019221	-0.021095	-0.007975
16 C	0.004785	-0.004255	0.001985	-0.001766
17 C	0.026347	-0.007757	0.010932	-0.003219
18 C	0.011015	0.004158	0.004570	0.001725
19 H	-0.027871	0.016464	-0.011564	0.006831
20 C	0.002469	0.005402	0.001024	0.002241
21 H	0.031793	0.017849	0.013192	0.007406
22 C	0.01149	0.005908	0.004767	0.002451
23 H	0.028824	0.031962	0.011959	0.013262
24 H	0.041496	0.032905	0.017218	0.013653
25 H	0.041232	0.034747	0.017108	0.014418
26 S	**0.269272**	**0.464558**	**0.111729**	**0.192759**
27 H	0.051745	0.049809	0.021471	0.020667

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

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 N	0.036736	0.065793	0.015242	0.027299
2 C	0.081742	0.063029	0.033917	0.026153
3 C	0.051654	0.002207	0.021433	0.000916
4 C	0.011018	0.012601	0.004572	0.005228
5 N	**0.119842**	0.074825	**0.049726**	0.031047
6 H	0.115216	0.054562	0.047806	0.022639
7 C	0.03076	0.022228	0.012764	0.009223
8 C	0.001978	-0.017846	0.000821	-0.007405
9 H	0.047887	0.043664	0.019869	0.018117
10 H	0.027668	0.046823	0.011480	0.019428
11 H	0.045978	0.044091	0.019077	0.018294
12 C	-0.012554	0.002878	-0.005209	0.001194
13 H	0.057663	0.049766	0.023926	0.020649
14 H	0.043416	0.037474	0.018015	0.015549
15 C	-0.045247	-0.003367	-0.018774	-0.001397
16 C	-0.000932	-0.005785	-0.000386	-0.002432
17 C	0.03035	0.018302	0.012593	0.007594
18 C	0.014693	0.018511	0.006096	0.007681
19 H	-0.020654	0.041203	-0.008569	0.017096
20 C	0.000986	0.009061	0.000409	0.003759
21 H	0.03747	0.034043	0.015547	0.014125
22 C	0.013575	0.020089	0.005633	0.008335
23 H	0.036737	0.055896	0.015243	0.023192
24 H	0.046814	0.050131	0.019424	0.020801
25 H	0.047459	0.057791	0.019692	0.023979
26 H	0.065207	0.058572	0.027056	0.024303
27 O	0.114536	**0.143457**	0.047524	**0.059525**

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According to fukui indices, N5 is the most reactive site for nucleophilic attack and O27 is the site of electrophilic attack in the compound BMPO. In the compound BMPT, S26 is the site of both electrophilic and nucleophilic attack. Generally when we have a carbonyl group, the carbon will be made highly electron deficient, so it becomes the centre of nucleophilic attack. By the same reason the oxygen will be rich in electrons, so the electrophiles will prefer to go to the oxygen only.

 In the case of the sulphone derivative, the sulphur atom has 2 pairs of non-bonding electrons, not only that among sulphur and oxygen, oxygen is more electronegative, which makes the sulphur atom a nucleophilic center.(by contrast carbon doesn't have lone pairs). Among sulphur and oxygen sulphur will be ready to part with its pair rather than the oxygen, which also confirms the inhibition efficiency in the order of BMPT > BMPO.

CONCLUSION

The inhibition efficiency of two pyridazine derivatives, 5-benzyl-6-methyl pyridazine-3-thione (BMPT) and 5-benzyl-6-methyl pyridazine-3-one (BMPO) has been investigated by utilizing DFT quantum chemical approaches. The inhibition efficiency increase with the increase in E_{HOMO}, and decrease in E_{LUMO} and energy gap(ΔE). BMPT 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.   The parameters like hardness(η), Softness(S), dipole moment(μ), electron affinity(EA) ionization potential(IE), electronegativity(χ) and the fraction of electron transferred (ΔN) confirms the inhibition efficiency in the order of BMPT >BMPO. Fukui function shows the nucleophilic and electrophilic attacking sites in the BMPT and BMPO**.** Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

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