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Research Article

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A theoretical study of some barbiturates as corrosion inhibitors for mild steel

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ABSTRACT

The Density functional theory (DFT) study was performed on three barbiturates namely, 5-(3-phenylallylidene) pyrimidine-2,4,6-trione (PPT), 5-(2-hydroxybenzylidene) pyrimidine-2,4,6-trione (HPT) and 5-benzlidene pyrimidine-2,4,6-trione (BPT) at the B3LYP/6-31G(d,p) basis set level 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 is analyzed through the Fukui function and condensed softness indices in order to compare the possible sites for nucleophilic and electrophilic attacks. The obtained correlations and theoretical conclusions agree well with the experimental data reported.*

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

INTRODUCTION

Mild steel is an alloy form of iron, which undergoes corrosion easily in acidic medium. Acidic solutions are extensively used in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid descaling and oil wet cleaning etc.[1]. Corrosion of mild steel in acidic medium poses great economic challenges to industries that utilize mild steel produced equipments for the transportation and storage of substances that have corrosive properties[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]. Among several methods used in combating corrosion problems, the use of chemical inhibitors remain the most cost effective and practical method. Therefore, the development of corrosion inhibitors based on organic compounds containing nitrogen, sulphur and oxygen atoms are of growing interest in the field of corrosion and industrial chemistry as corrosion poses serious problem to the service lifetime of alloys used in industry[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].The inhibition efficiency has been closely related to the inhibitor adsorption abilities and the molecular properties for different kinds of organic compounds [7]. 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 [8].

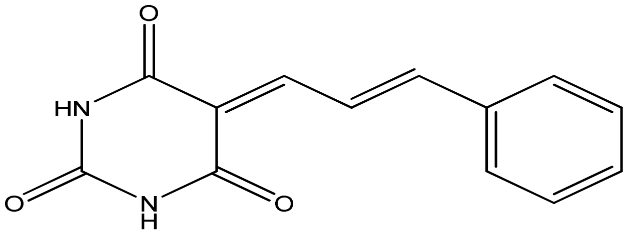
The geometry of an inhibitor also has an important influence in determining its adsorbability at the metal-solution interface. Molecules that are planar have a greater tendency to adsorb at the metal surface than molecule that has less planar geometry [9]. Quantum chemical calculations have been widely used to study reactive mechanism and also an effective tool in the analysis and elucidation of many experimental observations. They have been proved to be a very powerful tool for studying corrosion inhibition mechanism [10,11].

Electrochemical investigation of barbiturates as green corrosion inhibitors for mild steel protection was studied by Gulfeza Kardas, / Ramazan Solmaz [12]. Although experimental work of Quraishi *et al.* [13] provide valuable information on the corrosion inhibition efficiency of 5-(3-phenylallylidene) pyrimidine-2,4,6-trione (PPT), 5-(2-hydroxybenzylidene) pyrimidine-2,4,6-trione (HPT) and 5-benzlidenepyrimidine-2,4,6-trione (BPT) a deep understanding of the inhibition property remain unclear. The objective of the present paper is to extend the study of Quraishi *et al.* [13] by analyzing the inhibition efficiency of PPT,HPT and BPT 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.

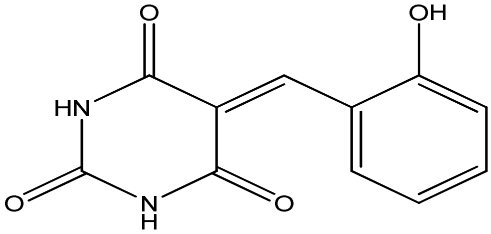
EXPERIMENTAL SECTION

2.1 Quantum Chemical Calculation

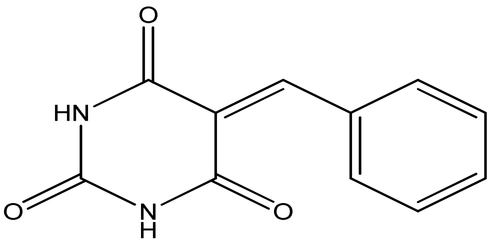
All the quantum chemical calculations have been performed at the B3LYP level of theory using Gaussian-03 series of programs [14]. The calculations were based on 6-31G (d,p) basis set. This method has been widely implemented to study the relationship between corrosion inhibition efficiency of the molecules and their electronic properties [15]. 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)[16] with the Becke's three parameter exchange functional along with the Lee– Yang–Parr nonlocal correlation functional (B3LYP) [17]. The chemical and optimized structures of the compounds studied are given in Fig 1. and Fig 2.



5-(3-phenylallylidene) pyrimidine-2,4,6-trione (PPT)

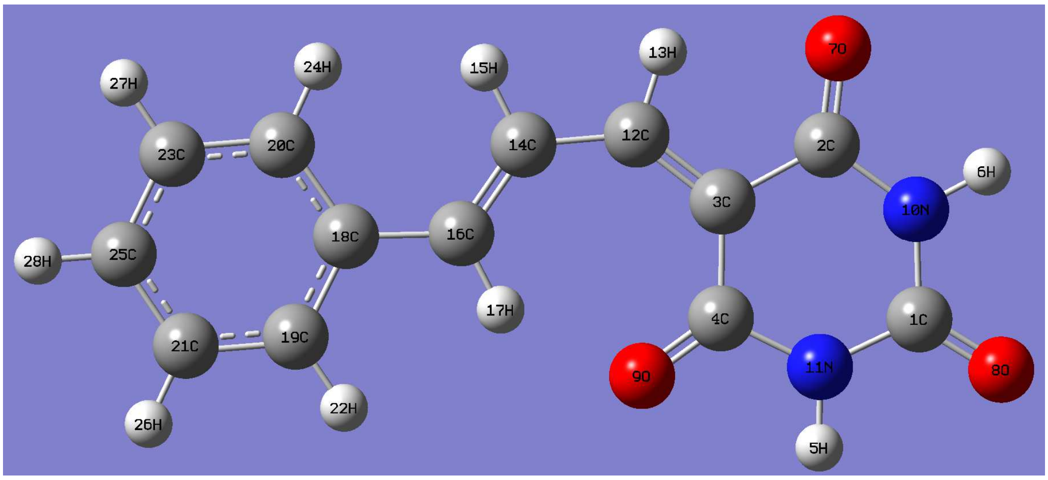


5-(2-hydroxybenzylidene) pyrimidine-2,4,6-trione
(HPT)

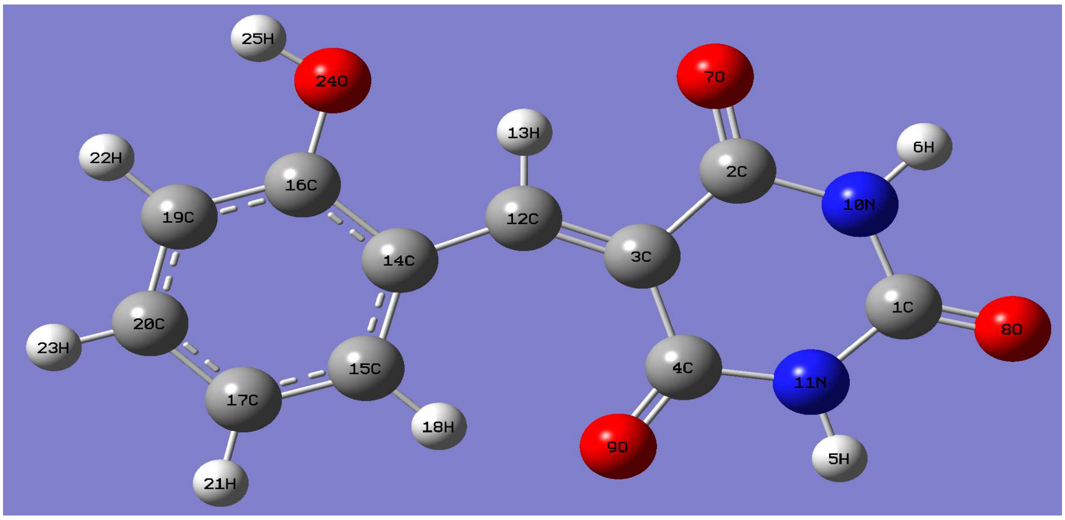


5-benzilidenepyrimidine-2,4,6-trione
(BPT)

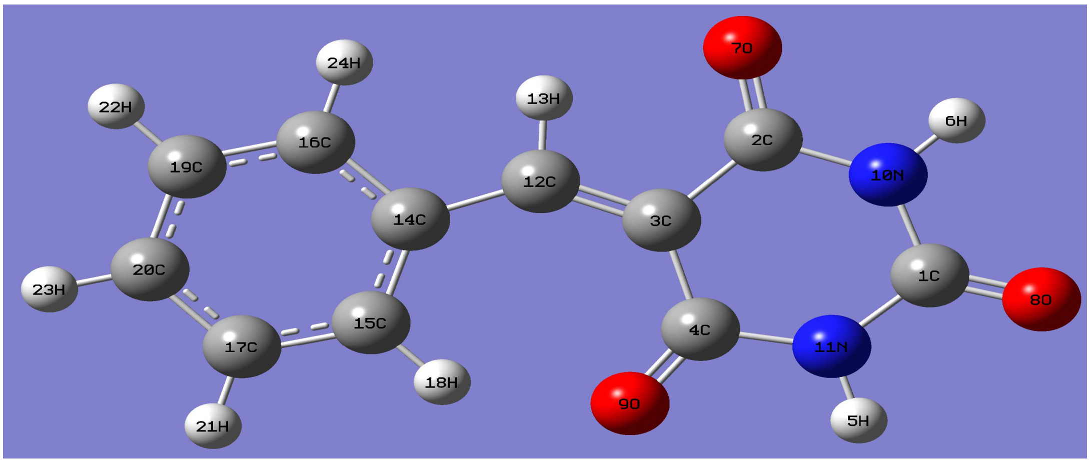
Figure 1. Names, molecular structure and the abbreviation of the inhibitors investigated



PPT



HPT



BPT

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

2.2. Theoretical background

Global quantities

Density functional theory (DFT) [16] 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.,* [18], 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 [19].

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

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

According to Koopman's theorem [20], 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 [21]. It is related to the energy of the E_{HOMO} through the equation:

$$I = -E_{HOMO} \tag{3}$$

Electron affinity (A) is defined as the energy released when a proton is added to a system [21]. It is related to E_{LUMO} through the equation:

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

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 [22], it can be estimated by using the equation:

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

Chemical hardness (η) measures the resistance of an atom to a charge transfer [23], it is estimated by using the equation:

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

Chemical softness (S) is the measure of the capacity of an atom or group of atoms to receive electrons [23], it is estimated by using the equation:

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

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 [24]. Therefore the fraction of electrons transferred (ΔN) from the inhibitor molecule to the metallic atom was calculated according to Pearson electronegativity scale [25]

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

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 [26] and η_{Fe} = 0 by assuming that for a metallic bulk I = A [27] 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* [28] 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.

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

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 [29]. 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 [30].

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

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

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 $s(r)$ [31].

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

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*., [32] 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.

$$\Delta E_{\text{Back-donation}} = -\frac{\eta}{4} \qquad (13)$$

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 [33]. 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 PPT, HPT and BPT is represented in fig. 3.

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

Parameters	PPT	HPT	BPT
E_{HOMO}(eV)	-6.3777	-6.4838	-6.9230
E_{LUMO} (eV)	-2.7359	-2.6317	-2.7754
Energy gap(ΔE) (eV)	3.6418	3.8521	4.1476
Dipole moment (Debye)	4.9462	5.3651	3.5726

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. E_{HOMO} facilitate adsorption and therefore inhibition by influencing the transport process through the adsorbed layer[34]. 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 E_{HOMO} for the three compounds follows the order; PPT>HPT>BPT which implies that PPT has the highest tendency to donate electrons.

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 [35]. Hard molecules have high HOMO-LUMO gap [36] and thus soft bases inhibitors are the most effective for metals [37]. The results as indicated in table 1 show that inhibitor PPT has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor.

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[38,39]

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 [40]. The low ionization energy 6.3777 (eV) of PPT 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) [16].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 [41]. In our present study PPT with low hardness value 1.8209(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 [42]. 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 [43]. PPT with the softness value of 0.54918 has the highest inhibition efficiency.

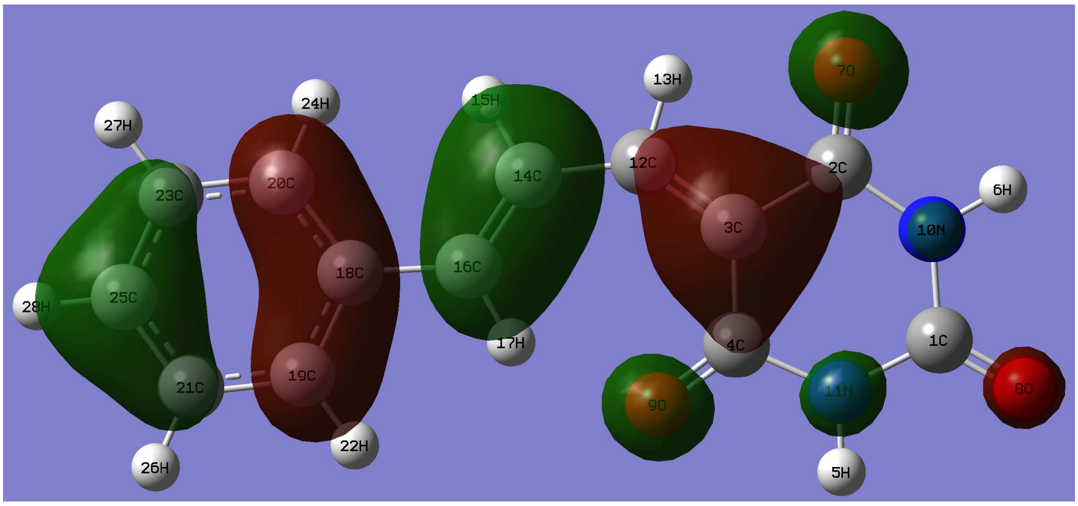
The table 2 shows the order of electronegativity as BPT>HPT>PPT. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order PPT>HPT>BPT. According to Sanderson's electronegativity equalization principle [44], with a high electronegativity and 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 PPT with high electrophilicity index value than the other compound, has the highest inhibition efficiency.

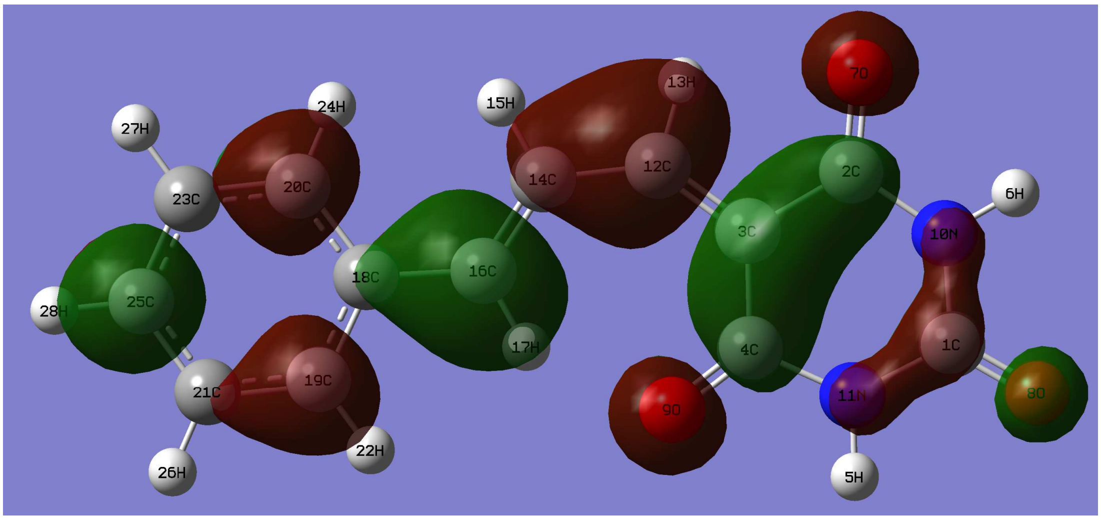
Table 2. Quantum chemical parameters for PPT,HPT and BPT calculated using B3LYP/6- 31G(d,p)

Parameters	PPT	HPT	BPT
IE(eV)	6.3777	6.4838	6.9230
EA(eV)	2.7359	2.6317	2.7754
η (eV)	1.8209	1.92605	2.0738
S (eV)	0.54918	0.51919	0.48220
χ (eV)	4.5568	4.55775	4.8492
ω	5.70169	5.39267	5.66948
μ	-4.5568	-4.55775	-4.8492

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 [45]. 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; PPT>HPT>BPT. 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 (PPT), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (BPT).



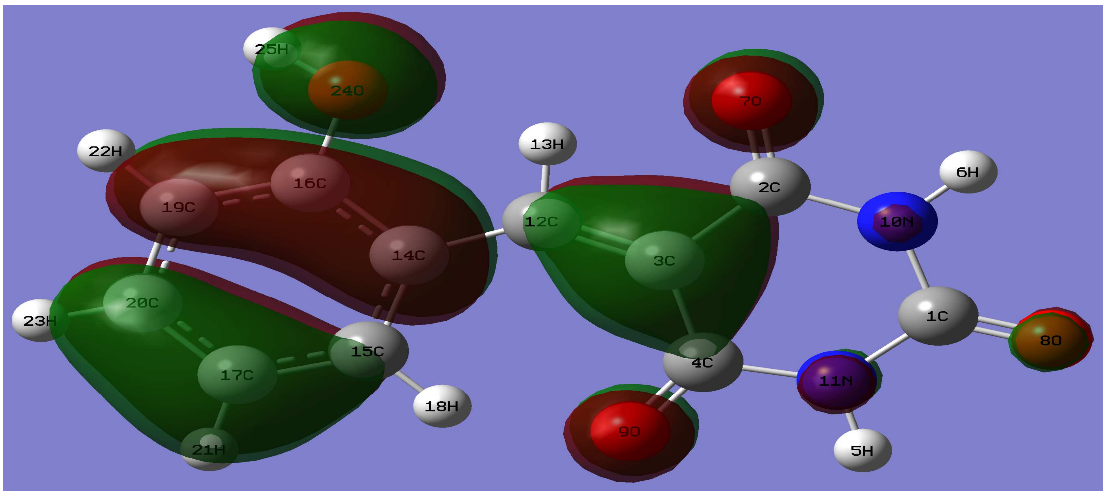
HOMO of PPT



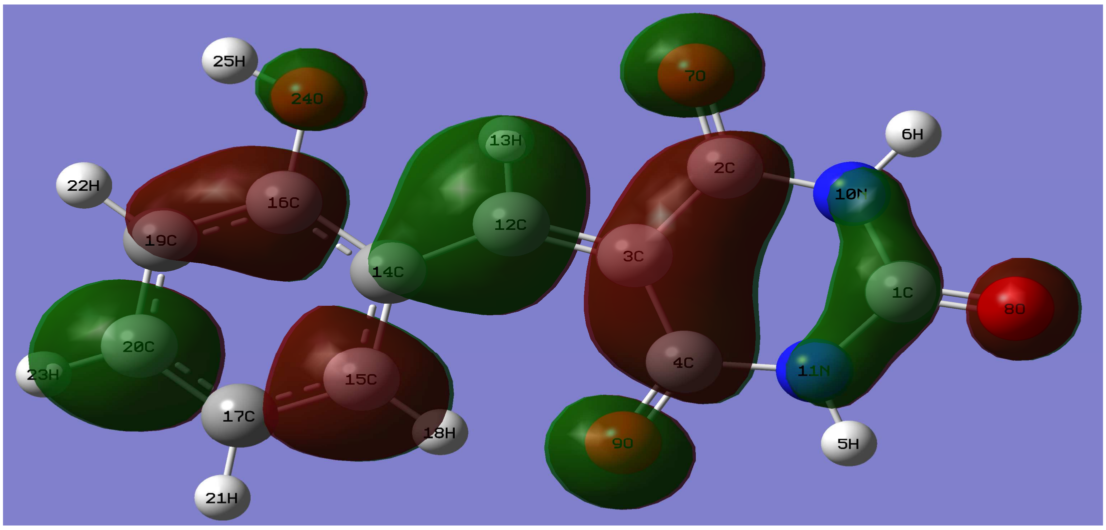
LUMO of PPT

Table 3. The number of electron transferred (ΔN) and ΔE back donation (eV) calculated for inhibitor PPT, HPT and BPT

Parameters	**PPT**	**HPT**	**BPT**
Transferred electrons fraction (ΔN)	0.67088	0.63400	0.51856
Back-donation ΔE / (eV)	-0.45522	-0.48151	-0.51845

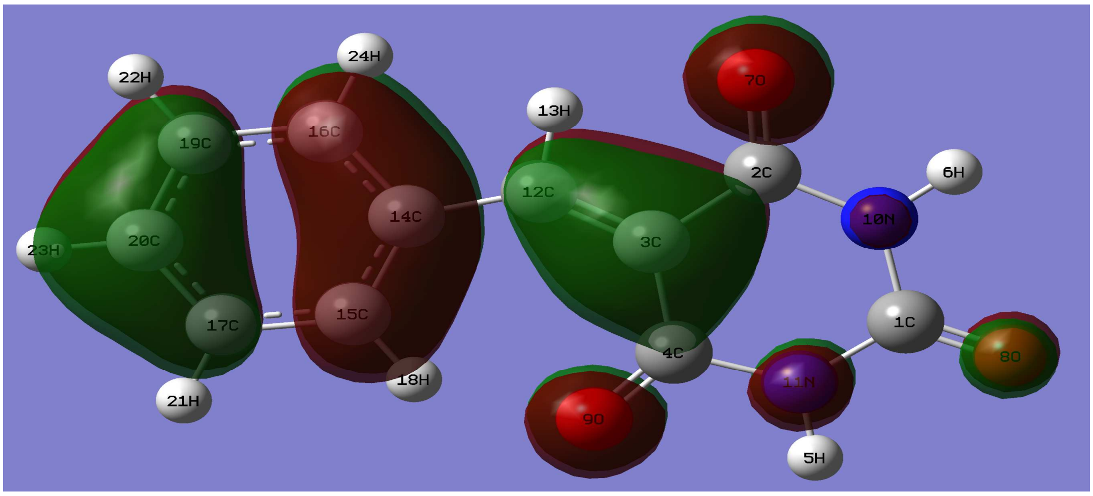


HOMO of HPT

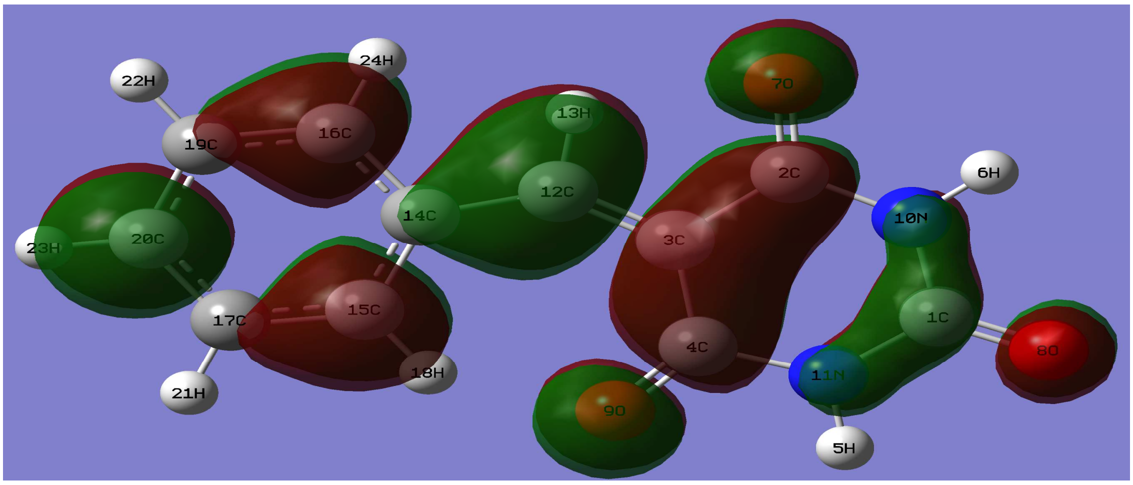


LUMO of HPT

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 [46]. 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 [32]. Parr and Yang proposed that larger value of Fukui function indicate more reactivity [47]. Hence greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule.



HOMO of BPT



LUMO of BPT

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

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 PPT,HPT and BPT presented in Tables 4,5 and 6.

According to fukui indices, O7 is the most reactive site for nucleophilic attack and H28 is the site of electrophilic attack in the compound PPT. In the compound HPT, C12 is the site of nucleophilic attack and O24 is the site of electrophilic attack. In the other compound BPT, O8 is the site of nucleophilic attack and C15 is the site of electrophilic attack.

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

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	0.031642	0.02253	0.017377	0.012373
2 C	0.056911	0.037443	0.031254	0.020563
3 C	0.00409	0.03981	0.002246	0.021863
4 C	0.06576	0.039158	0.036114	0.021505
5 H	0.03659	0.030829	0.020094	0.016931
6 H	0.038577	0.032428	0.021186	0.017808
7 O	**0.078517**	0.060231	**0.043119**	0.033077
8 O	0.076721	0.063469	0.042134	0.034856
9 O	0.057697	0.025978	0.031686	0.014266
10 N	-0.004568	0.000227	-0.002508	0.000125
11 N	-0.004789	0.003381	-0.002630	0.001857
12 C	0.04518	-0.001139	0.024812	-0.000626
13 H	0.060474	0.046209	0.033211	0.025377
14 C	-0.006239	0.047538	-0.003426	0.026107
15 H	0.055208	0.058611	0.030319	0.032188
16 C	0.073161	0.020665	0.040178	0.011348
17 H	0.043593	0.043547	0.023940	0.023915
18 C	-0.01912	0.001545	-0.010500	0.000848
19 C	0.019578	0.040221	0.010752	0.022088
20 C	0.025234	0.036789	0.013858	0.020204
21 C	0.002153	0.0109	0.001182	0.005986
22 H	0.038001	0.051898	0.020869	0.028501
23 C	0.000784	0.009833	0.000430	0.005400
24 H	0.034023	0.047447	0.018685	0.026057
25 C	0.030224	0.037784	0.016598	0.020750
26 H	0.051572	0.061838	0.028322	0.033960
27 H	0.051261	0.061455	0.028151	0.033749
28 H	0.057765	**0.069375**	0.031723	**0.038099**

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

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C				0.011958
2 C	0.036166	0.023033	0.018777	0.020407
3 C	0.061741	0.039307	0.032055	0.021731
4 C	-0.009021	0.041856	-0.004684	0.020194
5 H	0.075708	0.038895	0.039307	0.016825
6 H	0.040097	0.032406	0.020818	0.017057
7 O	0.040942	0.032854	0.021256	0.026747
8 O	0.080813	0.051517	0.041957	0.033821
9 O	0.083654	0.065141	0.043432	0.017450
10 N	0.075967	0.033610	0.039441	0.000010
11 N	-0.005734	0.000021	-0.002977	0.000749
12 C	-0.006822	0.001444	-0.003542	0.003603
13 H	**0.090215**	0.006939	**0.046838**	0.015529
14 C	0.058077	0.029910	0.030153	0.012739
15 C	-0.033398	0.024537	-0.017339	0.012625
16 C	0.039738	0.024316	0.020632	0.028291
17 C	0.041528	0.054490	0.021561	0.017634
18 H	-0.001208	0.033965	-0.000627	0.025006
19 C	0.035275	0.048163	0.018314	0.015139
20 C	0.012564	0.029159	0.006523	0.013271
21 H	0.038086	0.025562	0.019774	0.039708
22 H	0.060104	0.076481	0.031205	0.037980
23 H	0.063477	0.073153	0.032956	0.039720
24 O	0.069973	0.076504	0.036329	**0.046392**
25 H	0.019382	**0.089354**	0.010063	0.024602
	0.032677	0.047385	0.016965	

Table 6. Fukui and local softness indices for nucleophilic and electrophilic attacks in BPT atoms calculated from Mulliken atomic charges ; Maxima in bold

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	0.03713	0.03020	0.017904	0.014564
2 C	0.06485	0.03869	0.031270	0.018657
3 C	-0.01079	0.03856	-0.005204	0.018596
4 C	0.07756	0.05803	0.037399	0.027983
5 H	0.04102	0.03688	0.019781	0.017787
6 H	0.04203	0.03625	0.020267	0.017478
7 O	0.08414	0.06802	0.040575	0.032801
8 O	**0.08580**	0.07577	**0.041375**	0.036537
9 O	0.07854	0.06218	0.037871	0.029985
10 N	-0.00571	-0.00246	-0.002755	-0.001188
11 N	-0.00668	-0.00194	-0.003224	-0.000935
12 C	0.08488	0.01652	0.040931	0.007966
13 H	0.06282	0.05643	0.030290	0.027212
14 C	-0.02340	-0.00629	-0.011286	-0.003036
15 C	0.03792	**0.08331**	0.018285	**0.040173**
16 C	0.02028	0.03858	0.009782	0.018605
17 C	0.00192	0.02049	0.000927	0.009882
18 H	0.03447	0.01853	0.016625	0.008934
19 C	0.00304	0.03280	0.001465	0.015817
20 C	0.03855	0.02848	0.018588	0.013736
21 H	0.06086	0.06659	0.029347	0.032112
22 H	0.06445	0.07511	0.031077	0.036218
23 H	0.07048	0.07343	0.033987	0.035409
24 H	0.05582	0.05579	0.026918	0.026902

CONCLUSION

The inhibition potentials of three barbiturates namely, 5-(3-phenylallylidene) pyrimidine-2,4,6-trione (PPT), 5-(2-hydroxybenzylidene) pyrimidine-2,4,6-trione (HPT) and 5-benzlidenepyrimidine-2,4,6-trione (BPT) has been elucidated using quantum chemical calculations based on density functional theory (DFT). The inhibition efficiency increase with the increase in E_{HOMO}, and decrease in energy gap(ΔE). PPT 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), electron affinity(EA) ionization potential(IE), electronegativity(χ) and the fraction of electron transferred (ΔN) confirms the inhibition efficiency in the order of PPT>HPT>BPT. Fukui function shows the nucleophilic and electrophilic attacking sites in the inhibitors**.** Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

REFERENCES

[1] S Chitra; K Parameswari ; M Vidhya; M Kalishwari and A Selvaraj , *Int J Electrochem Sci.*, **2011**, 6, 4593 – 4613.
[2] Mwadham M. Kabanda; Lutendo C Murulana; Eno E. Ebenso, *Int J Electrochem Sci.*, **2012**, 7 , 7179 – 7205.
[3] SS Abdel-Rehim; KF Khaled and NA Al-Mobarak , *Arabian J Chem.*, **2011**, 4, 333-337.
[4] F Bentiss ; M Lagrence; M Traisnel and JC Hornez , *Corros Sci,* **1999**, 41, 789-803.
[5] L Tang ; X Li ; L Li ; G Mu and G Liu, *Surf Coat Technol.*, **2006,** 201, 384-388.
[6] IB Obot and NO Obi-Egbedi , *Surface Review and Letters*, **2008**, 15(6), 903-910.
[7] SL Granese, *Corros.*, **1988**, 44**,** 322-327.
[8] P Udhayakala; A Maxwell Samuel; TV Rajendiran and S Gunasekaran, *J. Chem. Pharm. Res.,* **2013**, *5(8):142-153*
[9] P Liu; X Fang; Y Tang; C Sun and C Yao, *Materials Sci. and Appl.*, **2011**, 2,1268- 1272.
[10] J Vosta and J Eliasek, *Corros. Sci.*, **1971**, 11, 223-229.
[11] F Bentiss; M Lebrini and M Lagrenee, *Corros. Sci.*, **2005**, 47, 2915-2931.
[12] Gulfeza Kardas and Ramazan Solmaz, *Corros. Reviews*, **2011**, 24(3-4),151–172.
[13] MA Quraishi; KR Ansari; Dileep Kumar Yadav and Eno E. Ebenso,*Int. J. Electrochem. Sci.,* **2012,** 7, 12301 – 12315.

[14] MJ Frisch; GW Trucks and HB Schlegel *et al.* Gaussian 03, Gaussian, Inc.: Pittsburgh PA, **2003**.
[15] DC Young, **2001** A practical guide for applying techniques to realworld problems in Computational Chemistry (New York: JohnWiley & Sons Inc.) p. 630.
[16] P Hohenberg and W Kohn, *Phys. Rev*., **1964**,136, B864-B871.
[17] AD Becke, *J. Chem. Phys*., **1993**, 98, 1372-1377.
[18] RG Parr; RA Donnelly; M Levy and WE Palke, *J. Chem. Phys*. **1978,** 68, 3801-3807.
[19] RG Parr and RG Pearson, *J. Am. Chem. Soc*., **1983**, 105, 7512-7516.
[20] P Geerlings; F De Proft and W Langenaeker, *Chem. Rev*. **2003,** 103, 1793-1873.
[21] JB Foresman; A Frisch, Exploring Chemistry with Electronic Structure Methods. Gaussian, Inc., Pittsburg, PA (USA), **1995**.
[22] L Pauling, The Nature of the Chemical Bond. Cornell University Press, Ithaca, New York; **1960.**
[23] P Senet, *Chem. Phys. Lett*., **1997,** 275, 527-532.
[24] S Martınez, *Mater. Chem. and Phys*., **2002**, 77, 97-102.
[25] RG Pearson, *Inorg.Chem*., **1988**, 27, 734-740.
[26] VS Sastri and JR Perumareddi, *Corros. Sci*, **1997**, 53, 617-622.
[27] MJS Dewar and W Thiel, *J.Am.Che.Soc.*, **1977**, 99**,** 4899-4907.
[28] RG Parr; L Szentpaly and S Liu , *J.Am.Chem.Soc.*, **1999**, 121,1922-1924.
[29] AA Siaka; NO Eddy; SO Idris and L Magaji , *Research J. Appl. Sci*., **2011,** 6(7-120), 487- 493.
[30] MA Quijano; Pardav; A Cuan; MR Romo; GN Silva; RA Bustamante; AR Lopez and HH Hernandez, *Int. J. Electrochem. Sci.*, **2011**, 6, 3729-3742.
[31] H Wang; X Wang; H Wang; L Wang and A Liu, *J. Mol. Model*., **2007**, 13, 147-153.
[32] B Gomez; NV Likhanova; MA Dominguez-Aguilar; R Martinez-Palou; R Vela and J Gasquez, *J.Phy.Chem B*, **2006**, 110, 8928-8934.
[33] AY Musa; AH Kadhum; AB Mohamad; AB Rohoma and H Mesmari, J.Mol.Struct., **2010**, 969, 233-237.
[34] G Gece and S Bilgic, *Corros.Sci*., **2009**, 51, 1876-1878.
[35] IB Obot; NO Obi-Egbedi and SA Umoren, *Int. J. Electro Chem. Sci*., **2009**, 4, 863-877.
[36] MK Awad*;* MS Mustafa and MM Abo Elnga, *J.Mol.Struct.,* **2010**, 959(1-3), 66-74.
[37] X Li; S Deng; H Fu and T Li, *Electrochim. Acta*, **2009**, 54, 4089-4098.
[38] LM Rodrigez-Valdez; A Martinez-Villfane; D Glossman-Mitnik, *J.Mol.Struct.* (THEO CHEM), **2005**, 713, 65-70.
[39] A Stoyanova; G Petkova and SD Peyerimhoff, *ChemPhys.*,**2002**, 279,1-6.
[40] Sandip K Rajak; Nazmul Islam and Dulal C Ghosh, *J.Quantum information Science*, **2011**, 1, 87-95.
[41] NO Obi-Egbedi; IB Obot; MI El-Khaiary; SA Umoren and EE Ebenso, *Int. J. Electro Chem. Sci*., **2011**, 6, 5649-5675.
[42] EE Ebenso; DA Isabirye and NO Eddy, *Int. J. Mol. Sci*., **2010**, 11, 2473-2498.
[43] R Hasanov; M Sadikglu and S Bilgic, *Appl. Surf. Sci*. **2007**, 253**,** 3913-3921.
[44] P Geerlings and F De Proft, *Int. J. Mol. Sci.*, **2002**, 3, 276-309.
[45] I Lukovits; E Kalman and F Zucchi, *Corrosion*, **2001**, 57, 3-8.
[46] G Breket; E Hur and C Ogretir, *J.Mol.Stru*,**2002**, 578, 79-88.
[47] RG Parr and W Yang, *J. Am. Chem. Soc.*, **1984**, 106, 4049-4050.