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ISSN : 2231- 3176  
CODEN (USA): JCMMDA

## Theoretical approach to the corrosion inhibition efficiency of some pyrimidine derivatives using DFT method

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### ABSTRACT

The adsorption mechanism and inhibition performance of two pyrimidine derivatives 6-methyl-4-phenyl-4,5-dihydropyrimidine-2-thiol (THPT1) and 4,6-diphenyl 4,5-dihydropyrimidine-2-thiol (THPT2) were investigated as corrosion inhibitors using Density functional theory (DFT) at the B3LYP/6-31G(d,p) basis set level. The result showed that the theoretically calculated order of IE was found to be in close agreement with the experimental order. The calculated quantum chemical parameters correlated to the inhibition efficiency are  $E_{HOMO}$  (highest occupied molecular orbital energy),  $E_{LUMO}$  (lowest unoccupied molecular orbital energy), the energy gap( $\Delta E$ ), hardness( $\eta$ ), Softness( $S$ ), dipole moment( $\mu$ ), electron affinity(EA), ionization potential(IE), the absolute electronegativity ( $\chi$ ) and the fraction of electron transferred ( $\Delta N$ ). The local reactivity has been analyzed through the condensed Fukui function and condensed softness indices in order to compare the possible sites for nucleophilic and electrophilic attacks.

**Keywords:** Pyrimidine, reactivity, DFT, Fukui function, softness indices.

### INTRODUCTION

Corrosion of metals is a major industrial problem that has attracted many investigation and researches [1,2]. The use of inhibitors is one of the most practical methods to protect metals against corrosion, especially in acidic media[3]. Most efficient inhibitors are organic compounds containing electronegative functional groups and  $\pi$ -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 group, such as the functional group, molecular electronic structure, electronic density at the donor atom,  $\pi$  orbital character and the molecular

size [4-6]. A number of heterocyclic compounds containing nitrogen, oxygen and sulphur either in the aromatic or long chain carbon system have been reported to be effective inhibitors [7,8]. The planarity and the lone electron pairs in the hetero atoms are important features that determine the adsorption of molecules on the metallic surface [9]. The inhibition efficiency has been closely related to the inhibitor adsorption abilities and the molecular properties for different kinds of organic compounds [10-14]. 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.

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 [15-20]. Density functional theory (DFT)[21,22] has provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes [23-27]. A variety of chemical concepts which are now widely used as descriptors of chemical reactivity, e.g., electronegativity [24] hardness or softness quantities etc., appear naturally within DFT [21]. The Fukui function[26] representing the relative local softness of the electron gas, measures the local electron density/population displacements corresponding to the inflow of a single electron.

The reactive ability of the inhibitor is closely linked to their frontier molecular orbital (MO), including highest occupied molecular orbital, HOMO, and lowest unoccupied molecular orbital, LUMO, and the other parameters such as hardness and softness. Quantum chemical studies have been successfully performed to link the corrosion inhibition efficiency with molecular orbital (MO) energy levels for some kinds of organic compounds [28,29].

D.G. De Kowalewski *et al.* have investigated the experimental and DFT study of substituent effects on scalar J(13C, 13C) couplings in pyrimidines [30]. Synthesis and antifungal activities of some novel Pyrimidine derivatives were investigated by Li Sun *et al.*[31]

The pyrimidine derivatives investigated in the present work are:

6-methyl-4-phenyl-4,5-dihydropyrimidine-2-thiol (THPT1)

4,6-diphenyl 4,5-dihydropyrimidine-2-thiol (THPT2)

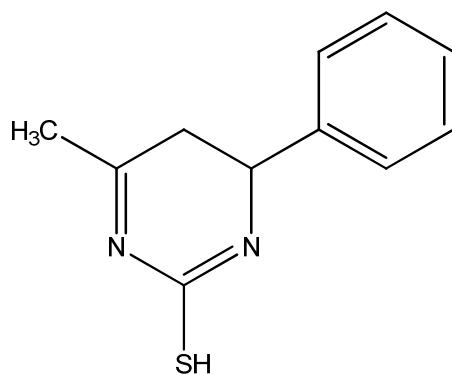
The object of the present study is to carry out a theoretical study on the electronic and structural parameters of two pyrimidine derivatives and the effect of these parameters on their inhibition efficiency of corrosion of mild steel using the quantum chemically calculated parameters. Results obtained showed that THPT1 < THPT2. It is well correlated with the experimental results [32]. From the calculations we will try to explain which adsorption site is favoured to bind to the metal surface. Computational calculations were obtained by means of B3LYP/6-31G(d,p) method. Parameters like  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , energy gap( $\Delta E$ ), dipole moment( $\mu$ ), global hardness( $\eta$ ), softness( $S$ ), the fraction of electron transferred ( $\Delta N$ ) and total energy change ( $\Delta E$ ) were calculated. 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.

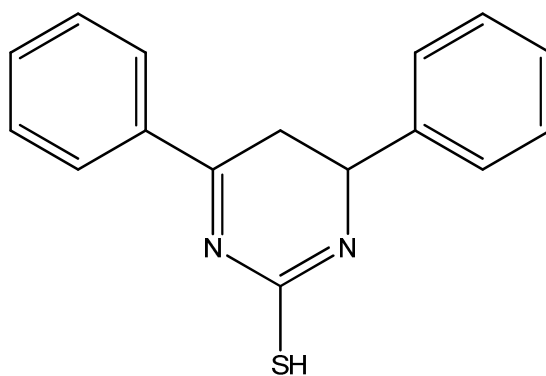
## MATERIALS AND METHODS

### Computational Details

In computational chemistry tools, the DFT offers the fundamentals for interpreting multiple chemical concept used in different branches of chemistry. In order to explore the theoretical-experimental consistency, quantum chemical calculations were performed with complete geometry optimizations using Gaussian-03 software package [33]. Geometry optimization were carried out by B3LYP functional at the 6-31G(d,p) basis set and at the density functional theory (DFT) level. 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 [34,35].

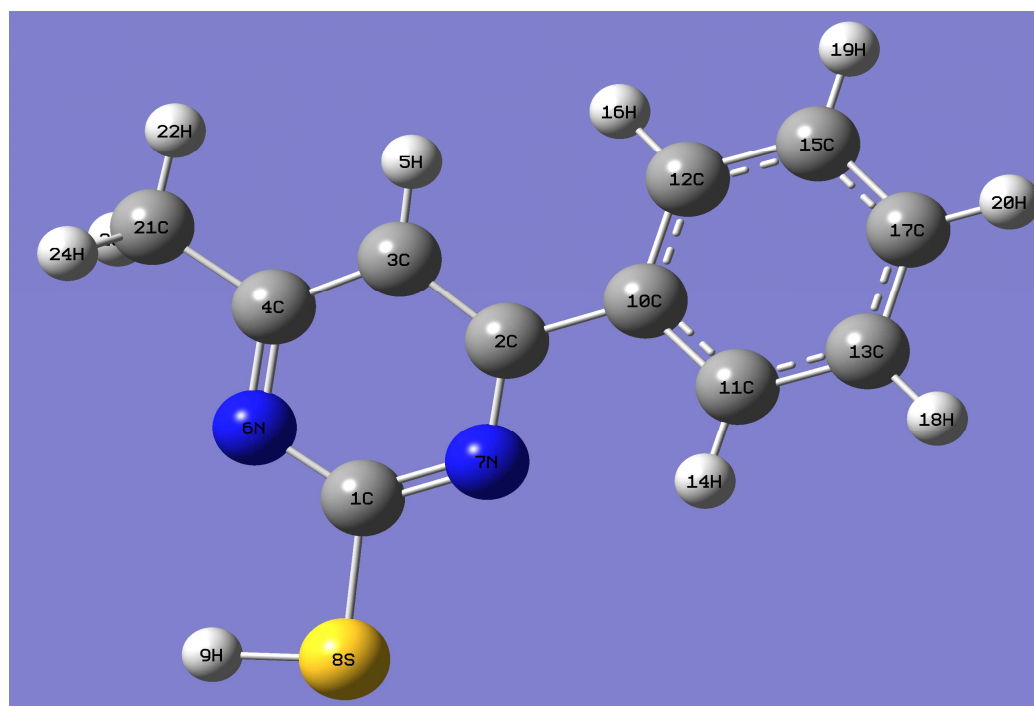
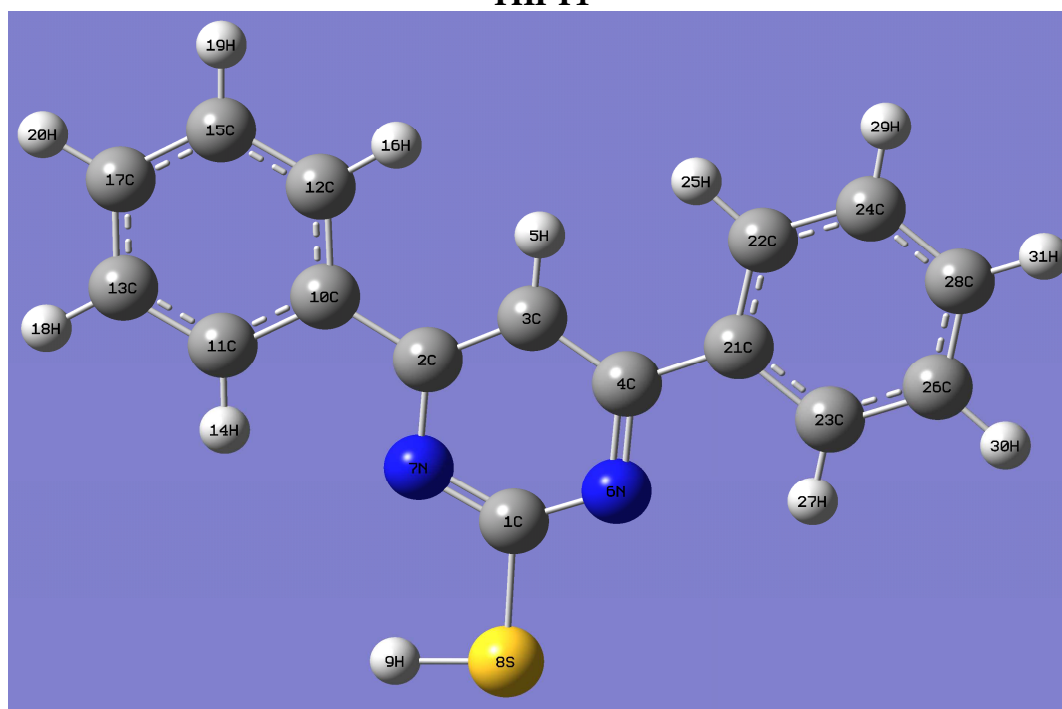


6-methyl-4-phenyl-4,5-dihydropyrimidine-2-thiol  
(THPT1)



4,6-diphenyl-4,5-dihydropyrimidine-2-thiol  
(THPT2)

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

**THPT1****THPT2****Figure 2.** Optimized structure of THPT1 and THPT2 calculated with the B3LYP/6-31G(d,p)

Density functional theory (DFT) [22] has been quite successful in providing theoretical basis for popular qualitative chemical concepts like electronegativity ( $\chi$ ), hardness ( $\eta$ ), softness (S) and local ones 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, Donnelly, Levy and Palke [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  $\chi$ .

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

Where  $\mu$  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 ( $\eta$ ) 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].

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

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

From the value of the total electronic energy, the ionization potential (IE) and electron affinity (EA) of the inhibitors are calculated using the following equations and hence  $\chi$  and  $\eta$  are calculated.

$$IE = E_{(N-1)} - E_{(N)}$$

$$EA = E_{(N)} - E_{(N+1)}$$

Where  $E$  is the total electronic energy,  $N$  is the number of electrons, and  $v(r)$  is the external electrostatic potential that the electrons feel due to the nuclei.

The higher HOMO energy corresponds to the more reactive molecule in the reactions with electrophiles, while lower LUMO energy is essential for molecular reactions with nucleophiles [38].

$$\chi = \frac{IE + EA}{2}$$

$$\eta = \frac{IE - EA}{2}$$

The global softness( $S$ ) is the inverse of the global hardness [37]

$$S = \frac{1}{\eta}$$

Electronegativity, hardness and softness have proved to be very useful quantities in the chemical reactivity theory. When two systems, Fe and inhibitor, are brought together, electrons will flow from lower  $\chi$ (inhibitor) to higher  $\chi$ (Fe), until the chemical potentials become equal. The number of transferred electrons ( $\Delta N$ ) was also calculated [39] by using the equation below.

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

Where  $\chi_{Fe}$  and  $\chi_{inh}$  denote the absolute electronegativity of iron and inhibitor molecule respectively  $\eta_{Fe}$  and  $\eta_{inh}$  denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of  $\chi_{Fe}=7.0$  eV and  $\eta_{Fe} = 0$  for the computation of number of transferred electrons[39]. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [40]. The local selectivity of a corrosion inhibitor is best analyzed by means of condensed Fukui function.

The global electrophilicity index was introduced by Parr[41] and is given by  $\omega = \mu^2/2\eta$ . 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  $\mu$ ,  $\omega$ ; and conversely a good electrophile is characterized by a high value of  $\mu$ ,  $\omega$ . This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge  $\Delta N$  from the environment.

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 [42].

$$f^+(r) = \rho_{N+1}(r) - \rho_N(r) \quad (\text{for nucleophilic attack})$$

$$f^-(r) = \rho_N(r) - \rho_{N-1}(r) \quad (\text{for electrophilic attack})$$

where  $\rho_{N+1}$ ,  $\rho_N$  and  $\rho_{N-1}$  are the electronic densities of anionic, neutral and cationic species respectively.

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  $s(r)$  [43]

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

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.

**RESULTS AND DISCUSSION**

The energy of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) measures the tendency towards the donation of electron by a molecule [44]. Therefore, higher values of  $E_{\text{HOMO}}$  indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on mild steel and therefore better inhibition efficiency.  $E_{\text{LUMO}}$  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 THPT1 and THPT2 is represented in figure 3.

**Table 1. Quantum chemical parameters for THPT1 and THPT2 calculated using B3LYP/6-31G(d,p).**

Parameters	THPT1	THPT2
$E_{\text{HOMO}}$ (eV)	-6.35739	-6.32011
$E_{\text{LUMO}}$ (eV)	-1.62043	-1.82397
Energy gap( $\Delta E$ ) (eV)	4.73695	4.49613
Dipole moment (Debye)	3.0878	3.2031

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[45].  $E_{\text{HOMO}}$  is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of  $E_{\text{HOMO}}$  is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy[46]. 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  $E_{\text{HOMO}}$  -6.32011 (eV) of THPT2 indicates the better inhibition efficiency than the other compound.

The energy gap, ( $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ ) is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As  $\Delta E$  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 [47]. Reportedly, excellent corrosion inhibitors are usually organic compounds which not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal [15]. A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule [48]. The results as indicated in table 1 shows that inhibitor THPT2 has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor.

The dipole moment ( $\mu$  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 the adsorption between chemical compound and metal surface [49]. The energy of the deformability increases with the increase in  $\mu$ , making the molecule easier to

adsorb at the Fe surface. The volume of the inhibitor molecules also increases with the increase of  $\mu$ . 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 3.2031 (Debye) of THPT2 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[50]. The low ionization energy 7.691744 (eV) of THPT2 indicates the high inhibition efficiency.

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[51]. In our present study THPT2 with low hardness value 3.69893 (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 [52]. 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[53]. THPT2 with the softness value of 0.270349 has the highest inhibition efficiency.

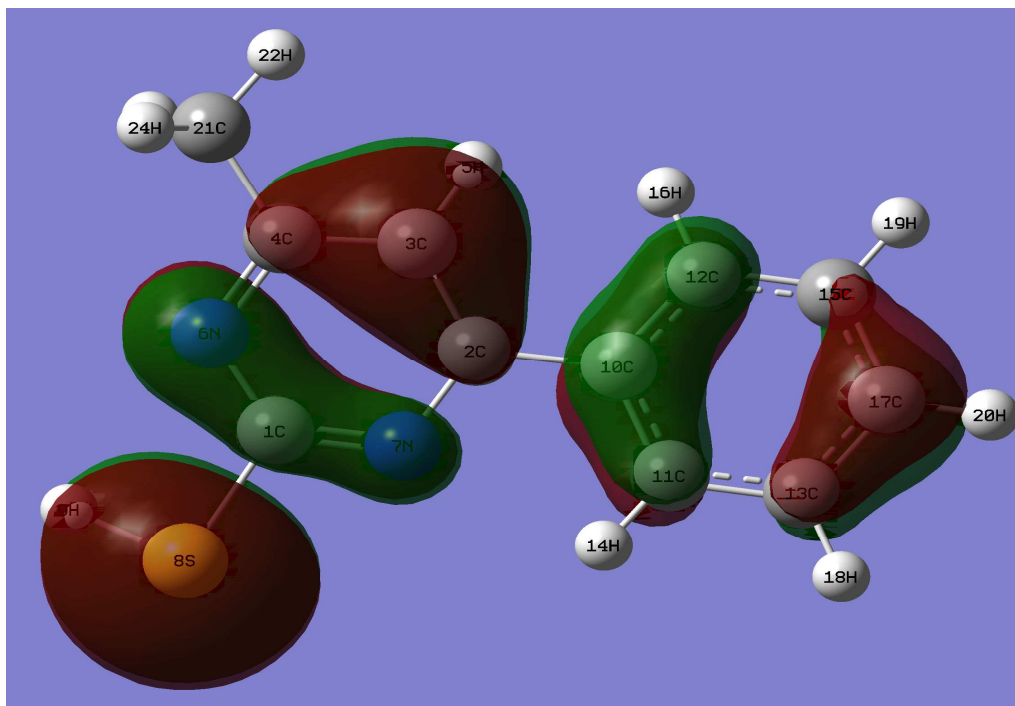
**Table 2. Quantum chemical parameters for THPT1 and THPT2 calculated using B3LYP/6-31G(d,p).**

Parameters	THPT1	THPT2
$E_N$ (au)	-932.91683	-1124.65944
$E_{N-1}$ (au)	-932.62594	-1124.37678
$E_{N+1}$ (au)	-932.92520	-1124.67024
IE(eV)	7.915699	7.691744
EA(eV)	0.227764	0.293889
$\eta$ (eV)	3.843968	3.69893
S (eV)	0.260147	0.270349
$\chi$ (eV)	4.071732	3.992817
$\omega$	2.15649	2.155027
$\Delta N$	0.3808791	0.406494

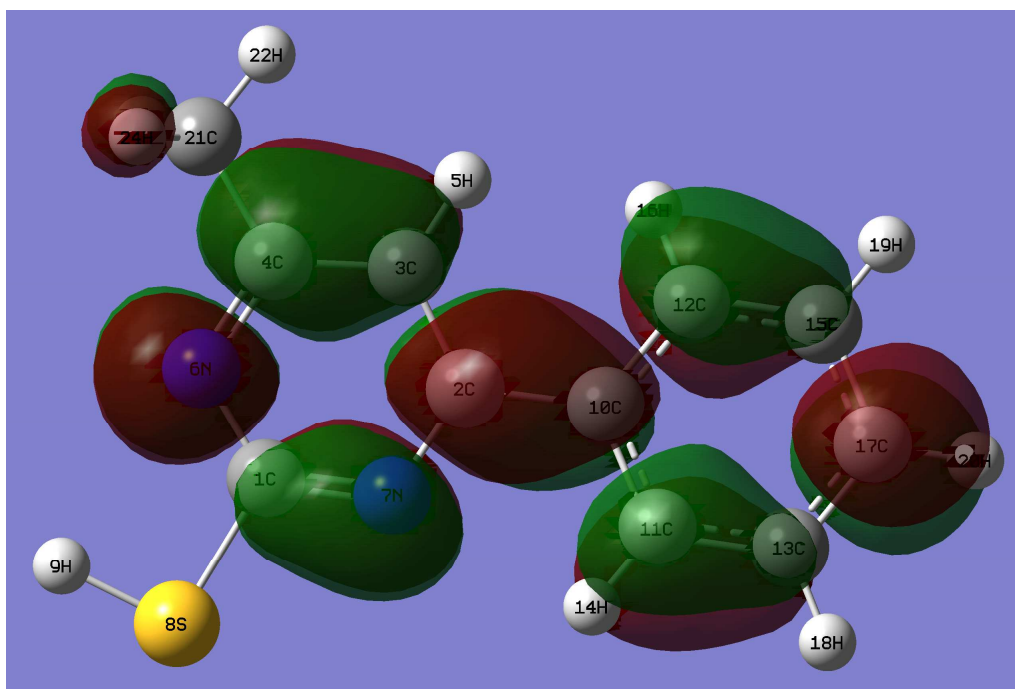
The table 2 shows the order of electronegativity as THPT1>THPT2. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order THPT2>THPT1. According to Sanderson's electronegativity equalization principle [54], THPT1 with a high electronegativity and low difference of electronegativity quickly reaches



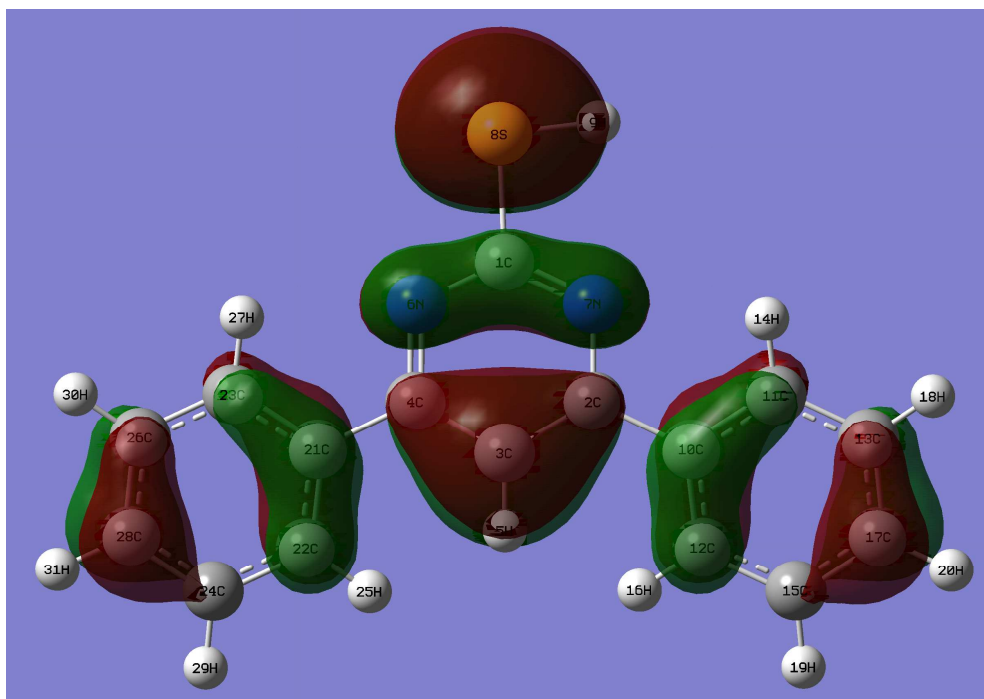
equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency.



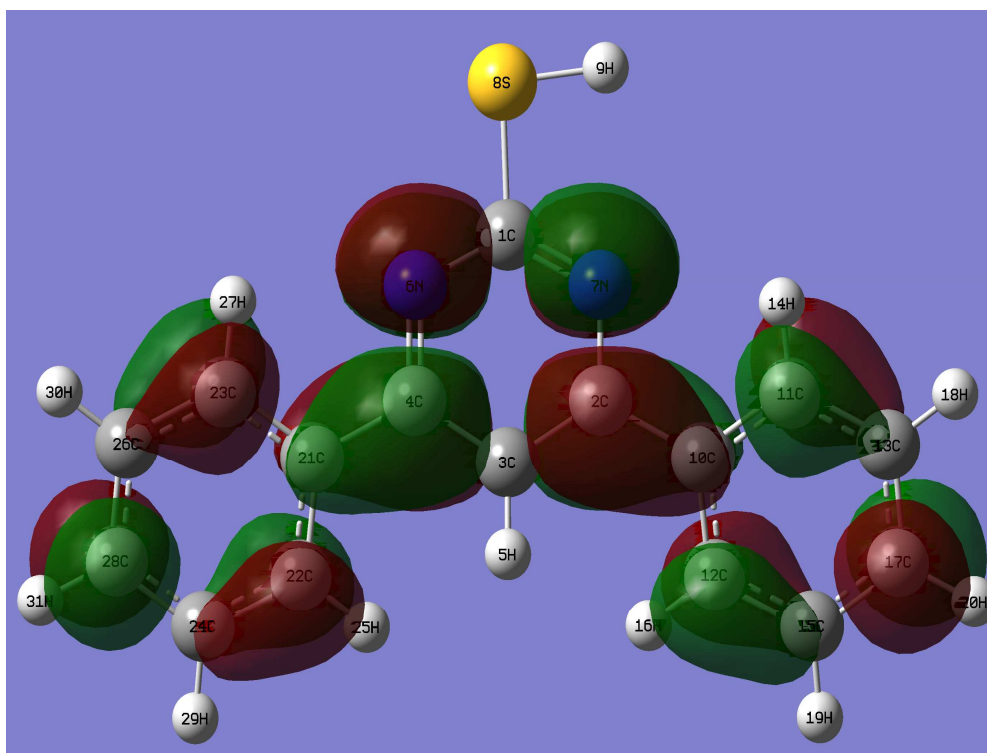
**HOMO of THPT1**



**LUMO of THPT1**



**HOMO of THPT2**



**LUMO of THPT2**

**Figure 3. Frontier molecular orbital diagrams of THPT1 and THPT2 by B3LYP/6-31G(d,p)**

**Table 3. Fukui and local softness indices for nucleophilic and electrophilic attacks on THPT1 atoms calculated from electron densities**

Atom No	$f_k^+$	$f_k^-$	$s_k^+$	$s_k^-$
1 C	<b>0.279201</b>	-0.272795	<b>0.072633</b>	-0.070967
2 C	-0.041532	-0.325397	-0.010804	-0.084651
3 C	-0.105991	0.563112	-0.027573	0.146491
4 C	0.182338	-0.363788	0.047434	-0.094638
5 H	0.093911	-0.110695	0.024430	-0.028797
6 N	-0.659347	<b>0.641576</b>	-0.171527	<b>0.166904</b>
7 N	-0.58736	0.496458	-0.152799	0.129152
8 S	0.035486	0.221105	0.009231	0.057519
9 H	0.081045	-0.088729	0.021083	-0.023083
10 C	0.071921	0.072083	0.018710	0.018752
11 C	-0.248613	0.116552	-0.064675	0.030320
12 C	-0.270051	0.167497	-0.070253	0.043573
13 C	-0.016018	0.086352	-0.004167	0.022464
14 H	0.128105	-0.122087	0.033326	-0.031761
15 C	-0.01429	0.064644	-0.003717	0.016816
16 H	0.093242	-0.087952	0.024256	-0.022880
17 C	-0.324598	0.249989	-0.084443	0.065033
18 H	0.090533	-0.093285	0.023551	-0.024268
19 H	0.087273	-0.089349	0.022703	-0.023244
20 H	0.103625	-0.097881	0.026957	-0.025463
21 C	-0.352478	0.367928	-0.091696	0.095715
22 H	0.110298	-0.112011	0.028693	-0.029139
23 H	0.131687	-0.142232	0.034257	-0.037001
24 H	0.131616	-0.141097	0.034239	-0.036706

The number of electrons transferred ( $\Delta N$ ) was also calculated and tabulated in Table 2. Values of  $\Delta N$  show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [55]. 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: THPT1 < THPT2. The results indicate that  $\Delta N$  values correlates strongly with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is associated with the best inhibitor (THPT2), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (THPT1).

There is a general consensus by several authors that the more negatively charged an heteroatom, is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction [15]. 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 [56]. Parr and Yang proposed that larger value of Fukui function indicate more reactivity [26]. Hence greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule. 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.

**Table 4. Fukui and local softness indices for nucleophilic and electrophilic attacks in THPT2 atoms calculated from electron densities.**

Atom No	$f_k^+$	$f_k^-$	$s_k^+$	$s_k^-$
C 1	<b>0.310692</b>	5.803948	<b>0.083995</b>	1.569091
C 2	0.036753	5.549713	0.009936	1.500359
C 3	-0.008743	6.228071	-0.002363	1.683752
C 4	0.044499	5.552945	0.012030	1.501233
H 5	0.096974	0.895332	0.026216	0.242052
N 6	-0.677285	7.316625	-0.183103	1.978042
N 7	-0.673789	7.318111	-0.182158	1.978444
S 8	0.038898	<b>15.967966</b>	0.010516	<b>4.316923</b>
H 9	0.079274	0.921908	0.021431	0.249236
C 10	0.086545	5.938665	0.023397	1.605512
C 11	-0.197257	5.987887	-0.053328	1.618819
C 12	-0.193911	6.031577	-0.052423	1.630630
C 13	-0.039405	6.145603	-0.010653	1.661457
H 14	0.116941	0.893837	0.031614	0.241647
C 15	-0.053327	6.138799	-0.014416	1.659618
H 16	0.088961	0.919145	0.024050	0.248489
C 17	-0.218553	5.932601	-0.059085	1.603872
H 18	0.090497	0.905873	0.024465	0.244901
H 19	0.089391	0.907901	0.024166	0.245450
H 20	0.098545	0.916127	0.026641	0.247674
C 21	0.086798	5.942532	0.023465	1.606557
C 22	-0.190183	6.035395	-0.051415	1.631663
C 23	-0.19494	5.993596	-0.052701	1.620362
C 24	-0.055518	6.137452	-0.015009	1.659254
H 25	0.08733	0.920382	0.023609	0.248824
C 26	-0.041831	6.143747	-0.011309	1.660955
H 27	0.125513	0.884819	0.033932	0.239209
C 28	-0.21078	5.939556	-0.056984	1.605753
H 29	0.088734	0.908654	0.023989	0.245653
H 30	0.091392	0.905116	0.024707	0.244697
H 31	0.097787	0.916117	0.026436	0.247671

The FMO diagram of THPT1 and THPT2 indicates the lack of electron cloud in LUMO near the thiol group in C1 showing the nucleophilic attack at the C1 site which is confirmed by the Fukui function  $f_k^+$ . In case of HOMO of THPT1 the dense electron cloud around N6 indicates the site of electrophilic attack. The same is the case around S8 in THPT2 as confirmed by the Fukui function  $f_k^-$  too.

## CONCLUSION

The following conclusions can be drawn from this study:

1. The inhibition efficiency of pyrimidine derivatives obtained Quantum chemically increase with the increase in  $E_{\text{HOMO}}$ , and decrease in  $E_{\text{LUMO}}$  and energy gap ( $\Delta E$ ). THPT2 has the highest inhibition efficiency because it had the highest HOMO energy and  $\Delta N$  values and it was most capable of offering electrons.
2. The parameters like hardness( $\eta$ ), Softness(S), dipole moment( $\mu$ ), electron affinity(EA) ionization potential(IE), electronegativity( $\chi$ ) and the fraction of electron transferred ( $\Delta N$ ) confirms the inhibition efficiency in the order of THPT2>THPT1.
3. Fukui function shows the nucleophilic and electrophilic attacking sites in the pyrimidine derivatives.

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