Theoretical Studies on the Efficiencies of Some Triazolopyrimidine Derivatives as Corrosion Inhibitors of Mild Steel in Acidic Medium Using AM1 and DFT Approach

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Authors' contributions

This work was carried out in collaboration between all authors. Author IAA designed the study and supervised the work. Author FKO wrote the protocol, preformed the statistical analysis, managed the literature search and wrote the first draft of the manuscript with assistance from author OFA. All authors read and approved the final manuscript.

Article Information

Review Article

ABSTRACT

A quantum chemical study of the efficiency of some Triazolopyrimidine derivatives as corrosion inhibitors of mild steel in H_2SO_4 was investigated. The AM1 semi-empirical method and Density Functional Theory (DFT) at the B3LYP/6-31G* level were used. The calculated quantum chemical parameters related to the inhibition efficiencies are the orbital energies (EHOMO and ELUMO), Separation Energy (ELUMO-EHOMO), Dipole moment (μ), Log P, Polarizability, Hardness (η) and Softness (S). A good correlation between the quantum chemical parameters and the experimental inhibition efficiency was observed. Quantitative Structure Activity Relationship (QSAR) approach was used on a composite index of some quantum chemical parameters to characterize the inhibition performance of the studied molecules. The results showed that the Inhibition Efficiency was closely related to some of the quantum chemical parameters. The calculated (theoretical)

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Inhibition Efficiency of the molecules was found to be close to their experimental Inhibition Efficiency. Results revealed that mol 2 (Pyrimidine thione) showed greater Inhibition Efficiency (IE) than the Pyrimidinones.

1. INTRODUCTION

The discovery and use of metals at the Stone Age was one of the most important steps in the development of modern technology. Most base metals are unfortunately not stable. In unfavorable environments they can be destroyed at variable rates by corrosion. The study of such corrosion reactions and the method by which corrosion of metals can be reduced is a task of great economic significance [1]. The use of chemical inhibitors to decrease the rate of corrosion processes is quite varied. In oil extraction and processing industries, inhibitors have always been considered to be the first line of defense against corrosion [2]. Thus inhibitors based on organic compounds containing hetero atoms such as Nitrogen, Sulfur and Oxygen atoms are of growing interest in the field of corrosion and Industrial Chemistry as corrosion poses serious threat to the life span of Metals/Alloys used in Industry. Organic heterocyclic compounds containing Azole nucleus have been found to be effective inhibitors for steel in different corrosive media [3]. Malki et al. [4], have studied the effect of addition of Triazoles and their derivatives on the corrosion of steel in 1 M HCl and 0.5 M H_2SO_4. They found that a high inhibition efficiency value is attributed to the electron density around Pyrazole Nitrogen. The inhibition efficiency of 3,5-bis(N-dihydropyridyl)-4-amino-1,2,4-triazoles has been reported [5]. Several Triazole derivatives have been synthesized and tested as effective inhibitors against Copper corrosion [6-9]. A review of literature reveals that triazolopyramidines have not been so far reported as inhibitors for acidic corrosion of Steel or Copper. Hence an attempt has been made to evaluate their corrosion inhibitive properties for mild steel. The efficiency of an organic inhibitor of metallic corrosion does not only depend on structural characteristics of the inhibitor but also on the nature of the metal and its environment. The selection of a suitable inhibitor for a particular system is a difficult task because of the selectivity of the inhibitors and a wide variety of environments.

In recent times Quantitative Structure Activity Relationship (QSAR) has been a subject of intense interest in many disciplines of Chemistry, particularly in the development of new corrosion inhibitors [10]. In this work we have studied the structural characteristics of Triazolopyrimidine derivatives with their corrosion inhibition efficiency in aqueous acidic solutions and to investigate the ability of quantum chemical calculations in selecting better corrosion inhibitors.

2. THEORETICAL METHOD

All the quantum chemical calculations were performed with SPARTAN'10 V1.0 [11]. The full optimization was initially achieved by using molecular mechanics force fields (MMFF). The results from MMFF were further selected as input and re-optimized using Semi empirical AM1. The Semi empirical AM1 structures were selected as input and were re-optimized using Density Functional Theory (DFT) at the level of B3LYP methods which uses the exchange functional proposal by Becke and all the correlations functional given by Lee, Yang and Parr [12-14]. The 6-31G* basis set has been used in conjunction with DFT method because it has the advantage of being flexible enough to guarantees reliable theoretical results and being small enough for rapid calculations. It represents an excellent compromise between completeness and economy. The molecular geometry was fully optimized without any constraint using analytical gradient procedure implemented within the program package. The following quantum chemical indices were considered: the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), separation energy ($E_{LUMO} - E_{HOMO}$), dipole moment (μ), Log P, and Polarizability of the various Triazolopyrimidine derivatives. Statistical analysis was performed using SPSS program version 17.0 for windows. Non-linear regression analysis was performed by unconstrained sum of squared residuals for loss function and estimation methods of Levenberg-Marquardt using SPSS program version 17.0 for windows [15]. The chemical structures and optimized geometry of triazolopyrimidine derivatives are shown in Figs. 1 and 2 respectively.
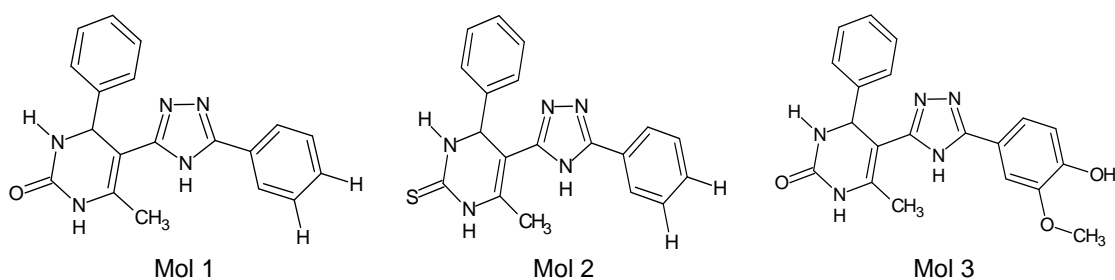
Fig. 1. Chemical structure of Inhibitors (mol 1 and 3. Triazole pyrimidinones, mol 2. Triazolopyrimidine thione)
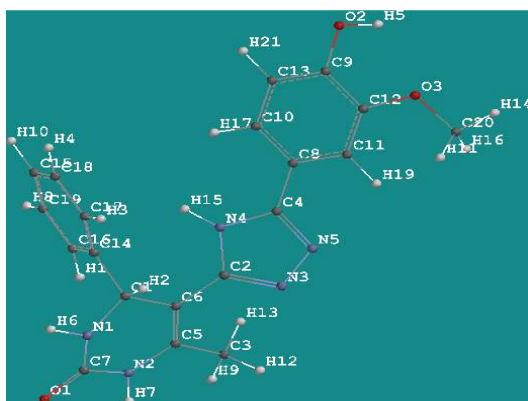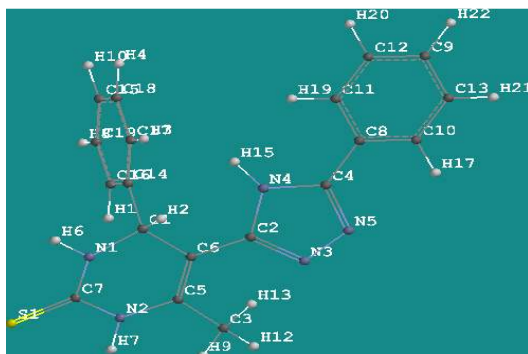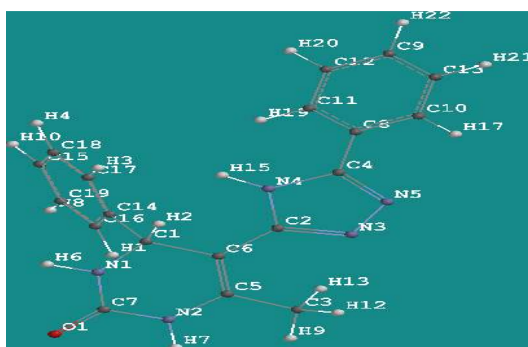

Fig. 2. Optimised structure of Inhibitors (mol 1 and 3. Triazole pyrimidinones, mol 2. Triazolopyrimidine thione)

3. RESULTS AND DISSCUSSION

Triazolopyrimidine derivatives (see Figs. 1 and 2) have been reported as corrosion inhibitor for steel in acidic medium, with inhibition efficiencies expressed as E_{exp} (%) based on the weight loss method for compounds 1 – 3 [16].

Table 1. Quantum chemical parameters of Triazolopyrimidine derivatives using AM1 method

Quantum chemical parameters	Mol 1	Mol 2	Mol 3
E_{Homo} (eV)	- 8.56	- 8.59	- 8.46
E_{Lumo} (eV)	- 0.51	- 0.78	- 0.53
$E_{Lumo - Homo}$ (eV)	8.05	7.81	7.93
Dipole moment (μ)	5.04	5.95	2.89
Log P	2.29	3.44	1.78
Polarizability	66.76	67.57	69.59
E_{exp} (%)	96.00	99.72	93.79

Table 2. Quantum chemical parameters of Triazolopyrimidine derivatives using DFT method

Quantum chemical parameters	Mol 1	Mol 2	Mol 3
E_{Homo} (eV)	- 5.47	-5.22	-5.23
E_{Lumo} (eV)	- 1.13	- 1.47	- 0.99
$E_{Lumo - Homo}$ (eV)	4.34	4.05	4.24
Dipole moment (μ)	4.92	5.94	3.39
Log P	0.70	1.84	-1.36
Polarizability	67.56	68.43	70.35
E_{exp} (%)	96.00	99.72	93.79

The E_{HOMO} is often associated with the electron donating ability of molecule [17-19]. Therefore, increasing values of E_{HOMO} indicates higher tendency for donation of electrons to the appropriate acceptor molecule with low energy and empty molecular orbital. Increasing values of E_{HOMO} facilitate the adsorption of the

inhibitor [20]. From Table 2, it is evident that mol 2 has the highest value of E_{HOMO}, which is consistent with the experimental % inhibition efficiency results which shows that the triazolopyrimidine thione (mol 2) is an excellent inhibitor as compared to pyrimidiones. The presence of sulfur atom in the thione enhances the efficiency as compared to the oxygen analogue. The E_{LUMO} indicates the ability of the molecule to accept electrons. Hence, the lower the value of E_{LUMO} the more apparent for the molecule to accept electrons. From Tables 1 and 2, mol 2 has the lowest value of E_{LUMO}.

Band gap: This indicates reactivity. The large energy gap (i.e larger value) indicates low reactivity to chemical specie because the energy gap is related to the softness or hardness of a molecule. A soft molecule is more reactive than a hard molecule because of larger energy gap [18,19]. From Tables 1 and 2, mol 2 has the lowest energy gap. Therefore, facilitate its effective interaction with the metal surface as compared to the other molecules, thus a better inhibitor which is consistent with experimental % inhibition efficiency results.

Log p: The values of log p (substituent constant) were also found to have a good relationship with the corrosion inhibition efficiencies of the studied inhibitors. Substituent constants are empirical quantities which account for the variation of the structure and do not depend on the parent structure but vary with the substituent [21]. Log p accounts for the Hydrophobicity of an actual molecule. Hydrophobicity of an organic molecule increases with decreasing water solubility. In corrosion studies, Hydrophobicity is related to the mechanism of formation of the oxide/ hydroxide layer on the metal surface which reduces the corrosion process drastically [20]. Hence increasing the value of log p increases the inhibition efficiencies of the thiazole molecules in the following order mol 2 > mol 1 > mol 3 which is consistent with experimentally obtained values of % inhibition efficiency.

Dipole moment (μ): This is useful for the prediction of the direction of a corrosion inhibition process. It is a measure of polarity in a bond and is related to the distribution of electrons in a molecule [22]. Although literature is inconsistent on the use of dipole moment as a predictor for the direction of a corrosion inhibition reaction, it is generally agreed that the adsorption of polar compounds possessing high dipole moments on

the metal surface should lead to better inhibition efficiency. Comparison of the results obtained from quantum chemical calculations with experimental inhibition efficiencies indicated that the % inhibition efficiencies of the inhibitors increases with increasing value of the dipole moment with mol 2 having the highest value of dipole moment.

Polarizability is the ratio of induced dipole moment to the intensity of the electric field. The induced dipole moment is proportional to polarizability [23]. The minimum polarizability principle (MPP) expects that the natural direction of evolution of any system is towards a state of minimum polarizability [19]. In Table 1, the trend for the increase in the inhibition efficiencies of the inhibitors with respect to increasing polarizability agrees with the order of the experimental % inhibition efficiencies results.

Table 3. Bond length and bond order of Triazolopyrimidine derivatives

Bond length (Å)	Mol 1	Mol 2	Mol 3
C_7=A	1.252	1.614	1.252
C_7–N_1	1.400	1.380	1.400
C_7–N_2	1.411	1.397	1.411
Bond order			
C=A	1.699	1.486	1.700
C_7–N_1	1.063	1.179	1.062
C_7–N_2	0.996	1.093	0.996

mol 1: A = O, mol 2: A = S, mol 3: A = O

The effect of substitution of the Oxygen atom by Sulfur atom attached to the Triazole moiety shows that the bond length C_7=S increases (1.614 Å) and accordingly the bond order decreases, (1.486) with respect to molecules 1 and 3. Also the bond lengths C_7–N_1 and C_7–N_2 decreases, (1.380Å) and (1.397Å) respectively and becomes stronger with bond order values, 1.179 and 1.093 respectively. This means the more weakening of the C_7=S with respect to C_7=O and accordingly increases its adsorption on the metal surface. Thus the triazolopyrimidine thione (mol 2) has the highest inhibition efficiency [24]. Correlations between the calculated quantum chemical parameters were also carried out as shown in Fig. 3. The figure reveals that the degree of linearity (R^2) between the plotted quantum chemical parameters and the experimental inhibition efficiencies were very close to unity, which indicated a high degree of linearity except for R^2 values of $E_{LUMO-HOMO}$ and Polarizability.
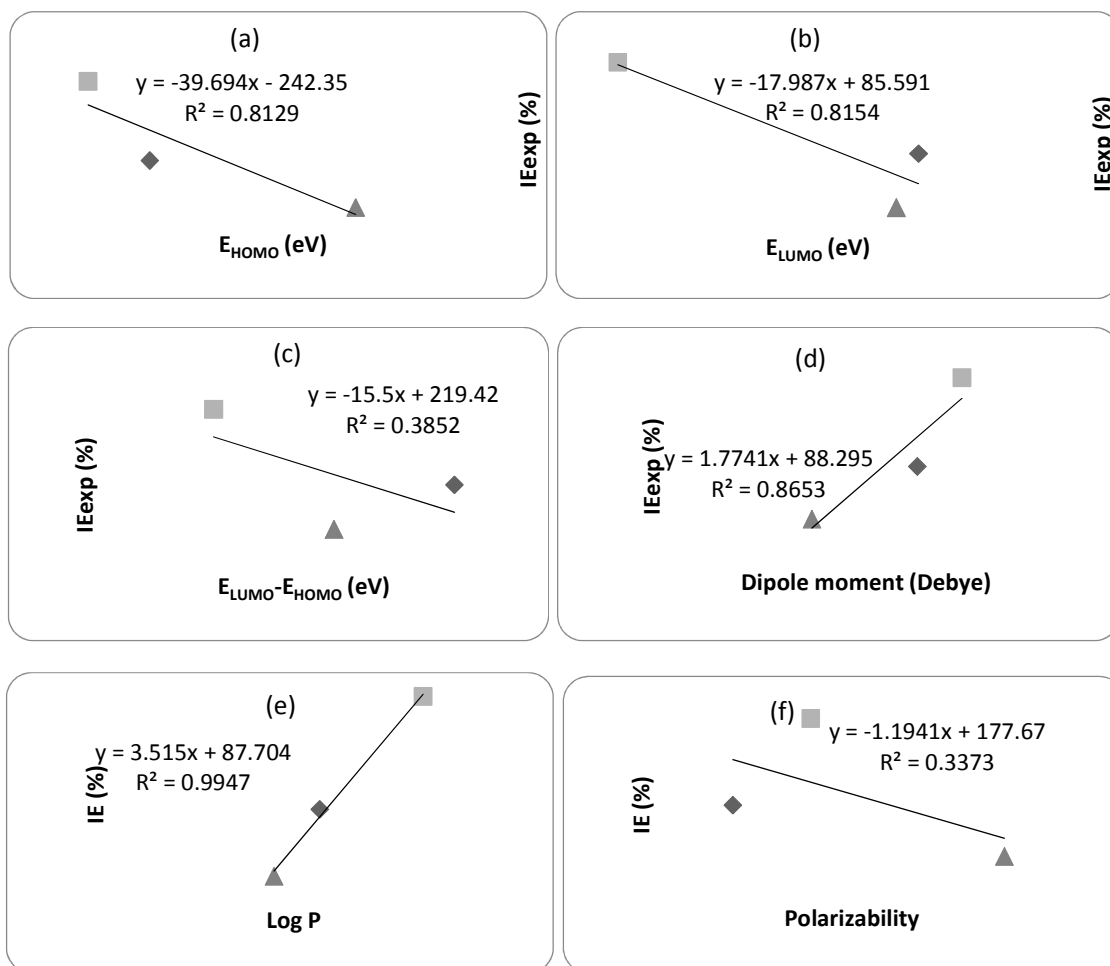
Fig. 3. Variation of experimental inhibition efficiency (IEexp) of the studied Triazolopyrimidines with (a) E_{HOMO} (b) E_{LUMO} (c) $E_{LUMO-HOMO}$ (d) Dipole moment (e) Log P and (f) Polarizability obtained from AM1 calculations

Table 4. Correlation coefficients, r (degree of linearity, R^2) between quantum chemical parameters and experimental inhibition efficiencies of the studied Triazolopyrimidines

Quantum parameter	Correlation coefficient (r)	Degree of linearity (R^2)
E_{HOMO}	0.901	0.812
E_{LUMO}	0.903	0.815
$E_{LUMO-HOMO}$	0.621	0.385
Dipole moment	0.930	0.865
Log P	0.997	0.994
Polarizability	0.581	0.337

According to Karelson and Lobanov [25], quantitative structure-activity and structure property relationship studies are of great importance in modern chemistry. The concept of QSAR/QSPR is to transform searches for compounds with desired properties using chemical intuition and experience into mathematically quantified and computed form. Once a correlation between structure and activity/relationship is found, any number of compounds including those not yet synthesized can readily be screened on the computer [26,27]. Most recent studies on the use of QSAR/QSPR for corrosion employ quantum chemical calculations as an attractive source of new molecular descriptor. According to Ebenso et al. [28], QSAR/QSPR can be used to relate the inhibition efficiency of most inhibitors to structural parameters, which can be theoretically calculated with the aim of obtaining a molecular design of new corrosion inhibitors, the development of

equations for calculating the corrosion inhibition efficiency has led to the prediction of the efficiency of inhibitors.

Attempts were made to establish the relationship between corrosion inhibition efficiencies and the calculated quantum chemical parameters using linear regression analysis. The linear model approximated the inhibition efficiency (IE_{Theor}) according to the following equation (1) [29].

$$IE_{Theor} = A_{x_i}C_i + B \qquad (1)$$

Where A, and B are the regression coefficients determined by regression analysis, x_i is a quantum chemical index, characteristic of the molecule i, C_i is the experimental concentration of the inhibitor.

Equation (1) did not give a good correlation between the experimental and theoretical inhibition efficiencies, thus a non-linear model

was adopted, which was first proposed by Lukovits et al. [30]. This model is based on the Langmuir adsorption isotherm (which assumes that the coverage of the metal surface by the inhibitor is the primary cause of corrosion inhibition). This is expressed in equation (2) [19].

$$IE_{Theor} = \frac{(A_{x_i}+B)C_i}{1+(A_{x_i}+B)C_i} \qquad (2)$$

Using the non-linear model, multiple regressions were performed between the inhibition efficiencies of the inhibitors and some quantum chemical parameters/descriptors. The solution of the non-linear model is given by equation (3).

$$IE_{Theor} = \frac{P^* C_I^* \, 100}{1+ P^* C_i} \qquad (3)$$

Where $P = E_{HOMO} - 16.470 E_{LUMO} + E_{LUMO-HOMO} + \mu + Log\, P - 0.897 Pol + 147.505$

Table 5. Theoretical inhibition efficiencies of the studied Triazolopyrimidines obtained from AM1 model

| Concentration (M)	IE_{Theor} (%)	IE_{Exp} (%)	IE_{Theor} (%)	IE_{Exp} (%)	IE_{Theor} (%)	IE_{Exp} (%)
0.02	67.29	50.08	68.42	66.39	66.21	51.09
0.04	80.44	65.94	81.25	82.29	79.67	68.18
0.06	86.05	73.77	86.67	89.18	85.46	75.44
0.08	89.16	76.86	89.66	96.22	88.68	80.91
0.10	91.14	80.02	91.55	98.75	90.74	82.29
0.15	93.91	83.31	94.20	99.15	93.63	86.69
0.25	96.26	87.40	96.44	99.16	96.08	89.92
0.50	98.09	93.81	98.19	99.43	98.00	92.62
1.00	99.04	96.00	99.09	99.72	98.99	93.79

y = 0.6177x + 37.377
R² = 0.8045
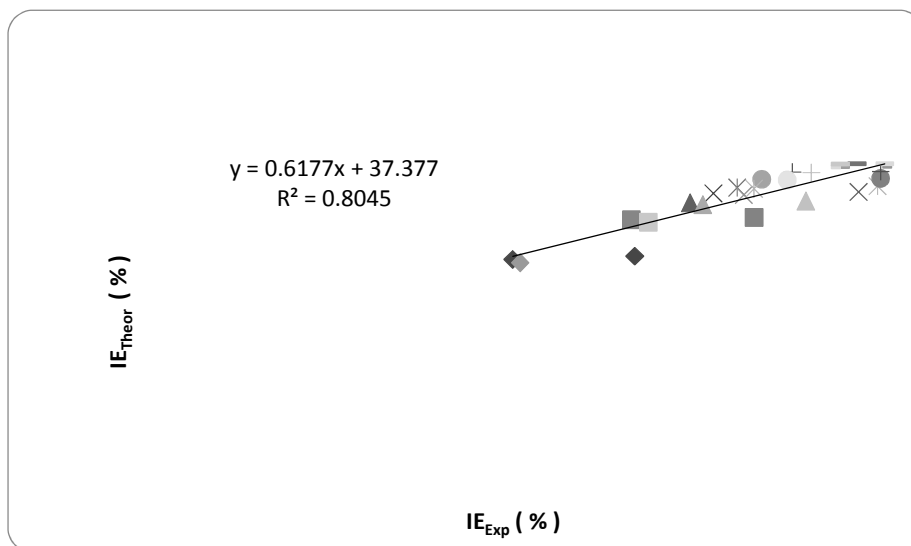
IE_{Theor} (%)

IE_{Exp} (%)

Fig. 4. Plot of calculated inhibition efficiencies (IE_{Theor}) obtained from equation (4) versus experimental inhibition efficiencies (IE_{Exp})

Table 6. Calculated quantum chemical descriptors for the studied Triazolopyrimidine derivatives using AM1 model

Inhibitor	E_N/ eV	$E_{(N-1)}$/eV	$E_{(N+1)}$/eV	IP/eV	EA/eV	S/eV^{-1}
Mol 1	4.62	11.95	2.82	7.33	1.80	0.1808
Mol 2	6.98	14.33	4.97	7.35	2.01	0.1873
Mol 3	1.06	8.32	-0.84	7.26	1.90	0.1866

Ionisation Energy and Electron Affinity:
Ionisation potential (IP) and Electron affinity (EA) were calculated using finite difference approximation as follows [31]:

$$IP = E_{(N-1)} - E_{(N)} \qquad (4)$$

$$EA = E_{(N)} - E_{(N+1)} \qquad (5)$$

Where $E_{(N-1)}$, $E_{(N)}$ and $E_{(N+1)}$ are the ground state energies of the system with N-1, N and N+1 electrons, respectively. Values of IP and EA are calculated from equations 4 and 5 and are presented in Table 6. Thus indicating that the inhibition efficiencies of the inhibitors increase with increasing value of ionization energy but decreases with decreasing value of electron affinity. This is because IP is directly related with the E_{HOMO} and EA is directly related with E_{LUMO}. This explains why the trend for the variation of inhibition efficiencies of the inhibitors with IP and EA are similar to those obtained for E_{HOMO} and E_{LUMO} data. Using the finite difference approximation, the global softness and hardness can be calculated as follows:

$$S = \frac{1}{(E_{(N-1)} - E_{(N)}) - (E_{(N)} - E_{(N-1)})} \qquad (6)$$

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

The calculated values of S and η are also presented in Table 6, it is evident that the inhibitor with the least value of global hardness or the highest value of global softness is the best and vice versa. This is because a soft molecule is more reactive than a hard molecule. Comparison of the results obtained from quantum chemical calculations with experimental inhibition efficiencies indicated that the % inhibition efficiencies of the inhibitors increases with increasing value of the softness and decreasing value of hardness, with mol 2 having the highest value of softness and lowest value of hardness. This observation is consistent with the results obtained from experimental % inhibition efficiencies.

4. CONCLUSION

A comparison of the inhibition effectiveness of some Triazolopyrimidine derivatives indicates that their inhibition effect is closely related to orbital energies (E_{HOMO} and E_{LUMO}), Energy band gap (E_{LUMO}-E_{HOMO}), Dipole moment (μ), Log P, Polarizability, Softness(S) and Hardness(η). The inhibition efficiency of the Triazolopyrimidine derivatives increases with increasing E_{HOMO}, decreasing E_{LUMO}, decreasing E_{LUMO}-E_{HOMO}, increasing Dipole moment, increasing Log P, increasing Polarizability, increasing Softness and decreasing Hardness. Thus indicating that mol 2 (Pyrimidine thione) showed greater Inhibition Efficiency (IE) than the Pyrimidinones, as observed with the experimental results. A high significant coefficient of determination (R^2 = 0.804) was obtained between experimental and calculated inhibition efficiencies.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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