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QUANTUM CHEMICAL CALCULATION FOR THE INHIBITORY EFFECT OF COMPOUNDS

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The effects of the molecular structure on the corrosion inhibition efficiency are investigated by nine methods of calculations. The selected thio compounds were previously identified as corrosion inhibitors for mild steel in the 1.0 M HCl solution. The electronic properties such as highest occupied molecular orbital (EHOMO) energy, lowest unoccupied molecular orbital (ELUMO) energy, dipole moment (μ), and Fukui indices are calculated and discussed. Results show that the corrosion inhibition efficiency increase with the increase in both EHOMO and μ values, respectively, and decrease in ELUMO. QSAR approach is utilized in this study; a good relationship is found between the experimental corrosion inhibition efficiency ($IE_{Exp}\%$) and the theoretical corrosion inhibition efficiency ($IE_{Theo}\%$). The calculated inhibition efficiency is found closer to the experimental inhibition efficiency with a coefficient of correlation (R^2) of 0.875.

Keywords: corrosion inhibition, quantum chemical parameter, thio, QSAR.

Corrosion is the destructive attack of metal or alloy chemically or electrochemically against its environment which leads to the loss of useful properties of materials. The protection of metals against corrosion can be achieved by adding inhibitors in small concentrations to its environment [1]. Corrosion inhibitor can effectively reduce the corrosion rate of metallic materials in acid solution and has been widely applied in acidic cleanout, crude oil refiner, electrochemical and chemical etching [2]. Organic compounds, mainly containing oxygen, nitrogen and sulfur atoms and having multiple bonds, are recognized as effective inhibitors of the corrosion of many metals and alloys [3]. The protection of metal surfaces against corrosion is an important industrial and scientific issue. Inhibitors are one of the practical means of preventing corrosion, particularly in acidic media. Inhibitors can adhere to a metal surface to form a protective barrier against corrosive agents in contact with metal [4]. The effectiveness of an inhibitor to provide corrosion protection depends to a large extent on the interaction between the inhibitor and the metal surface.

The most efficient corrosion inhibitors are organic compounds containing electronegative functional groups and π electrons in their triple or conjugated double bonds [5]. Some thio compounds have been found to be good inhibitors for mild steel in acid [6—8]. Recently theoretical chemistry, such as quantum chemical calculations [9, 10], has been used to explain the mechanism of corrosion inhibition. Quantum chemical calculations are proved to be a very powerful tool for studying the inhibition mechanism [11, 12].

The objective of this study is to determine the relationship between the corrosion inhibition efficiency and the molecular structures of the nine previously studied thio compounds (contains double

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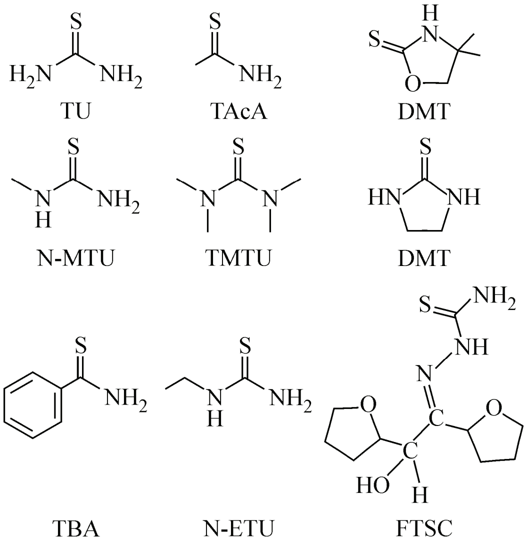

Fig. 1. Structures of the tested compounds

bond S atom) namely: thiourea (TU) [13], thioacetamide (TAcA) [14], 4,4-dimethyloxazolidine-2-thione (DMT) [15], N-methylthiocarbamide (N-MTU) [14], tetramethylthiocarbamide (TMTU) [14], 2-imidazolidinethione (ETU) [14], thiobenzamide (TBA) [13], N-ethylthiocarbamide (N-ETU) [13], thiocarbamide (TCA) [14] and Schiff base furointhiosemicarbazone (FTSC) [16].

The structural parameters, such as the frontier molecular orbital MO energy HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) and dipole moment were calculated and correlated with corrosion inhibition efficiencies. The calculated values of inhibition efficiencies ($\mathrm{IE_{cal}}\%$) were obtained from quantitative structure-activity relationship (QSAR) and were correlated with the values of experimental inhibition efficiencies ($\mathrm{IE_{exp}}\%$). The values of $\mathrm{IE_{exp}}\%$ were obtained experimentally by polarization measurements. The molecular structures for the selected thio compounds are shown in Fig. 1.

EXPERIMENTAL

Theory and computational details. The molecular sketches of nine thio compounds were plotted using Visualization Materials Studio 5.5. All quantum chemical calculations were performed using Density Functional Theory (DFT) in Materials Studio 5.5 software. $\mathrm{DMol^3}$ model was employed to obtain quantum chemical parameters and to optimize the molecules geometry. These calculations employed an *ab initio*, Local Density Approximations (LDA) with the Perdew-Wang (PWC) functional and Double Numerical d-functions (DND) basis set. This approach is shown to yield favorable geometries for a wide variety of systems. The following quantum chemical indices were calculated: the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), dipole moment (μ) and Fukui indices.

The condensed Fukui functions can also be employed to determine the reactivity of each atom in the molecule. The corresponding condensed functions are given by

$$f_k^+ = q_k(N+1) - q_k(N) \quad \text{(for nucleophilic attack)}$$

$$f_k^- = q_k(N) - q_k(N-1) \quad \text{(for electrophilic attack)}$$

$$f_k^0 = [q_k(N+1) - q_k(N-1)]/2 \quad \text{(for radical attack)}$$

where q_k is the gross charge of atom k in the molecule. The N corresponds to the number of electrons in the molecule. $N+1$ corresponds to an anion, with an electron added to the LUMO of the neutral molecule. $N-1$ correspondingly is the cation with an electron removed from the HOMO of the neutral molecule. These quantities were calculated using Mulliken Population Analysis.

QSAR approach was carried out utilizing non-linear regression analyses implemented in Materials Studio 5.5 software. The non-linear regression analyses were performed by an unconstrained sum of squared residuals for loss function and estimation methods of Genetic Function Approximation.

RESULTS AND DISCUSSION

Density functional theory (DFT) has recently been used to analyze the characteristics of the inhibitor/surface mechanism and to describe the structural nature of the inhibitor in the corrosion process. Furthermore, DFT is considered to be a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data. DFT has been found to be successful in provi-

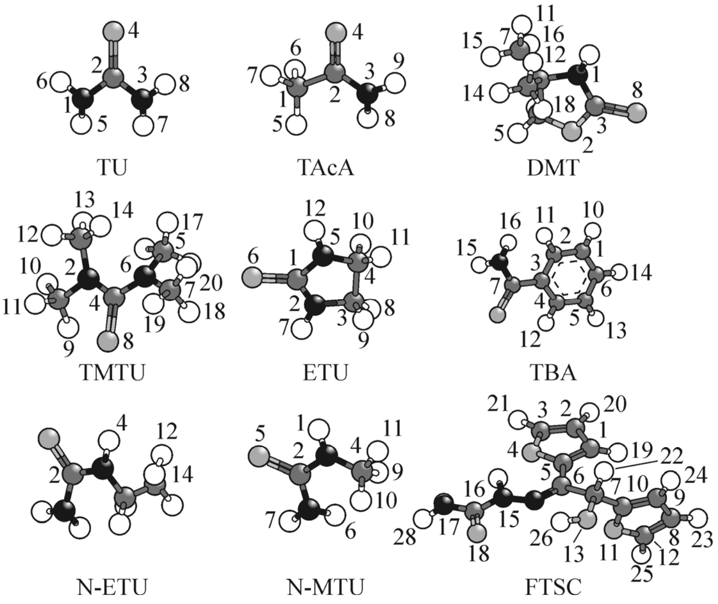

Fig. 2. 3D structures of the tested compounds

ding insights into chemical reactivity and selectivity, in terms of global parameters such as electronegativity (v), hardness (g) and softness (S), and local ones such as the Fukui function (*f* ð ~ *r* Þ) and local softness (*s* ð ~ *r* Þ) [17, 18].

The choice of some of these compounds, used as corrosion inhibitors is based on the facts that, first, these molecules have sulfur and nitrogen (in addition to the azomethine group) as active centers, and the azomethine group has biological activities as antibacterial and antifungal. The mode of action of the tested compounds may involve the formation of a hydrogen bond through the azomethine group (>C=N—) with the active centers of various cellular constituents, resulting in interference with normal cellular processes. Interference with the synthesis of cellular walls causes damage that can lead to altered cell permeability characteristics or disorganized lipoprotein arrangements, ultimately resulting in cell death) [19—22]. The second fact is that these compounds can be easily synthesized and characterized [23, 24].

QUANTUM CHEMICAL CALCULATIONS

The optimized molecules structures of the selected thio molecules are shown in Fig. 2.

The calculated quantum parameters of HOMO, LUMO and dipole moment for the selected thio compounds are presented in Table 1.

Table 1

Molecular properties of the optimize thio compounds using DMol^3

Compound	HOMO, eV	LUMO, eV	Dipole moment, debye	Concentration, mM	IE$_{\text{Exp}}$, %	IE$_{\text{Theo}}$, %
TU	–4.720	–1.142	1.929	0.05	18	38.3
	–4.720	–1.142	1.929	0.4	48.6	45.73
TAcA	–4.561	–1.654	1.601	0.001	56	44.66
	–4.561	–1.654	1.601	10	67	74.18
DMT	–4.849	–1.220	2.222	0.4	35.2	31.17
	–4.849	–1.220	2.222	4	82.5	80.37
N-MTU	–4.550	–0.726	1.975	0.001	63	65.34
	–4.550	–0.726	1.975	10	92	94.86
ETU	–4.606	–0.870	1.904	0.001	67	56.92
	–4.606	–0.870	1.904	10	92	86.44
TMTU	–4.404	–1.062	1.599	0.001	71	69.43
	–4.404	–1.062	1.599	10	95	98.95
N-ETU	–4.504	–0.700	2.012	0.001	68	66.92
	–4.504	–0.700	2.012	10	95	96.44
TBA	–4.860	–2.602	1.487	0.001	48	57.78
	–4.860	–2.602	1.487	10	97	87.3
FTSC	–4.819	–2.626	3.101	0.1	71.1	67.14
	–4.819	–2.626	3.101	3	97.7	98.4

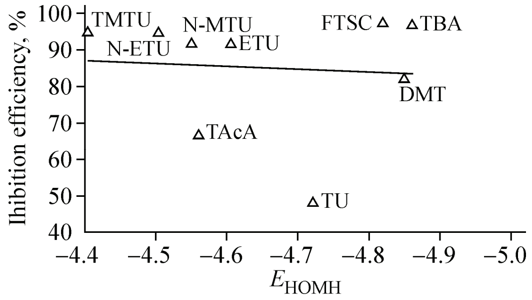

Fig. 3. Correlation of HOMO energy with percent inhibition efficiency of thio compounds

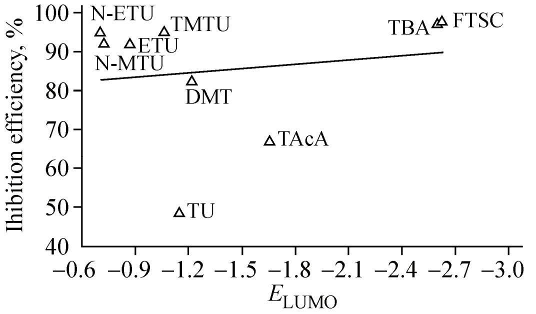

Fig. 4. Correlation of LUMO energy with percent inhibition efficiency of thio compounds

Frontier orbital theory is useful in predicting adsorption centers of the inhibitor molecules responsible for the interaction with surface metal atoms [25]. Terms involving the frontier molecular orbital could provide dominative contribution, because of the inverse dependence of stabilization energy on orbital energy difference. Reportedly, excellent corrosion inhibitors are usually those organic compounds which not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal [26, 27].

A relationship between corrosion inhibition efficiency of these thio compounds with orbital energies of HOMO (E_{HUMO}), LUMO (E_{LUMO}) and dipole (μ) are shown in Figs. 3, 4 and 5 respectively. As clearly seen in these figures, the inhibition efficiency is increased with increases in E_{HOMO} and μ decreases with E_{LUMO} values.

The E_{HOMO} is often associated with the electron donating ability of a molecule. Therefore, increasing values of E_{HOMO} indicates a higher tendency for the donation of electron(s) to the appropriate acceptor molecule with low energy and empty molecular orbital. Increasing values of E_{HOMO} facilitate the adsorption of the inhibitor. Consequently, the inhibition efficiency of the inhibitor would be enhanced by improving the transport process through the adsorbed layer. This can be explained as follows the E_{LUMO} indicates the ability of the molecule to accept electrons. Therefore, the lower the value of E_{LUMO} the more apparent it is that the molecule would accept electrons [28]. The dipole moment (μ) is an index that can also be used for the prediction of the direction of a corrosion inhibition process. The dipole moment is the measure of polarity in a bond and is related to the distribution of electrons in a molecule. Although the literature is inconsistent on the use of (μ) 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. The data obtained from the present study indicates that the FTSC inhibitor has the highest values of μ (3.101) and highest inhibition efficiency (97.7 %).

The dipole moment is another indicator of the electronic distribution in a molecule. Authors state that the inhibition efficiency increases with increasing value of the dipole moment (which depends on the type and nature of molecules considered) but in some cases no significant relationship has been found between the dipole moment values and the %IE. Besides, there is a lack of agreement in the literature on the correlation between the dipole moment and %IE [29—33].

The calculated Fukui indices for the charged species ($N+1$ and $N-1$) as well as the neutral specie (N) are listed in Table 2. For simplicity, only the Fukui functions over the nitrogen (N), oxygen (O) and sulfur (S) are presented. For a finite system such as an inhibitor molecule, when the molecule is accepting electrons

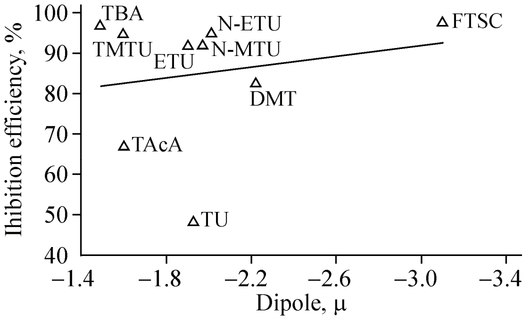

Fig. 5. Correlation of dipole moment (μ) energy with percent inhibition efficiency of thio compounds

Table 2

Fukui indices parameters for N, O *and* C *atoms of the studied thio compounds*

Molecule	Atom	f^+	f^-	f^0	Molecule	Atom	f^+	f^-	f^0
TU	O(4)	0.026	–0.012	0.007	TMTU	N(2)	0.042	–0.011	0.015
	O(11)	–0.01	–0.011	–0.01		N(5)	0.012	0.018	0.015
	O(13)	0.038	0.025	0.032		S(8)	0.321	0.517	0.419
	N(14)	0.084	–0.074	0.005	N-ETU	N(1)	0.06	0.025	0.042
	N(15)	0.006	0.017	0.011		N(3)	0.061	0.004	0.033
	N(17)	0.027	0.017	0.022		S(6)	0.371	0.61	0.491
	S(18)	0.162	0.519	0.341	TBA	S(8)	0.27	0.52	0.395
TAcA	N(3)	0.099	0.028	0.063		N(9)	0.058	0.024	0.041
	S(4)	0.421	0.614	0.518	FTSC	O(4)	0.026	–0.012	0.007
DMT	O(2)	0.074	0.02	0.047		O(11)	–0.01	–0.011	–0.01
	N(4)	0.064	0.019	0.041		O(13)	0.038	0.025	0.032
	S(8)	0.402	0.606	0.504		N(14)	0.084	–0.074	0.005
N-MTU	N(1)	0.064	0.022	0.043		N(15)	0.006	0.017	0.011
	N(3)	0.044	0.017	0.031		N(17)	0.027	0.017	0.022
	S(5)	0.388	0.603	0.496		S(18)	0.162	0.519	0.341
ETU	N(2)	0.049	0.009	0.029					
	N(5)	0.049	0.009	0.029					
	S(6)	0.391	0.615	0.503					

which has f^+, the index for nucleophilic attack; when the molecule is donating electrons, which has f^-, the index for electrophilic attack. The site for nucleophilic attack is the site where the value of f^+ is maximum, while the site for electrophilic attack is controlled by the values of f^-. Assuming that the protonated forms of the inhibitors molecules have a net positive charge, and as the sulfur atom exhibits the highest value Fukui indices (Table 2) in the all studied thio compounds, **it** can therefore be deduced that the sites for nucleophilic and electrophilic attack are the sulfur atoms (S 18), (S 4), (S 8), (S 4), (S 5), (S 6), (S 8), (S 6), (S 9) and (S 18), for the inhibitors (TU), (TAcA), (DMT), (TCA), (N-MTU), (ETU), (TMTU), (N-ETU), (TBA) and (FTSC) respectively.

Quantitative structure activity relationship (QSAR). QSAR was used to correlate the inhibition efficiency of these inhibitors and their molecular structure. The QSAR approach is adequately sufficient to forecast the inhibitor effectiveness using a theoretical approach; it may be used to find the optimal group of parameters for predicting a molecule′s suitability to be a corrosion inhibitor. However, it may be used to find the optimal group of quantum chemical parameters that might predict the structure and molecule′s suitability to be an inhibitor. Attempts are made to find a relationship between the experimental inhibition efficiencies and some quantum chemical parameters [9, 34]. The following proposed regression analysis was used to correlate inhibitor concentration (C_i) and LSER parameters with the experimental inhibition efficiencies $E_{\text{exp}}\%$. The linear model approximates corrosion inhibitor efficiency ($E_{\text{cal}}\%$) as in Eq. (1) [35]

$$E_{\text{cal}}\% = Ax_jCi + B, \tag{1}$$

where A and B are constants obtained by regression analysis, x_j is a quantum chemical index (E_{HOMO}, E_{LUMO} and μ) characteristic for the molecule j, Ci denotes the inhibitor concentration. Such a linear approach was not found to be satisfactory for the correlation of the present results. The non-linear model (NLM) proposed by Lukovits *et al.* [36] for the study of interaction of corrosion inhibitors with the metal surface in acidic solutions has been used in this work according to the following Eq. (2):

$$E_{\text{cal}}\% = \frac{(Ax_j + B)C_i}{1 + (Ax_j + B)C_i} \times 100, \tag{2}$$

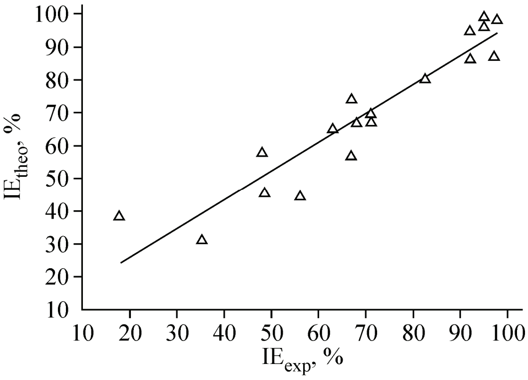

Fig. 6. Correlation of experimental and calculated inhibition efficiencies of thio compounds

where A and B are the regression coefficients determined by regression analysis, x_j is a quantum chemical index characteristic for the molecule j, and C is the experimental concentration of the inhibitor i. The application of the above non-linear approach to the present situation did not give a good correlation between the experimental and theoretical inhibition efficiencies, where it gave the coefficient of correlation ($R^2 = 0.278$).

Consequently, the non-linear model (NLM) was performed by the unconstrained sum of squared residuals for the loss function and estimation methods of Genetic Function Approximation. The relationship as represented in Eq. (3) has a good coefficient of correlation ($R^2 = 0.887$), as shown in Fig. 6.

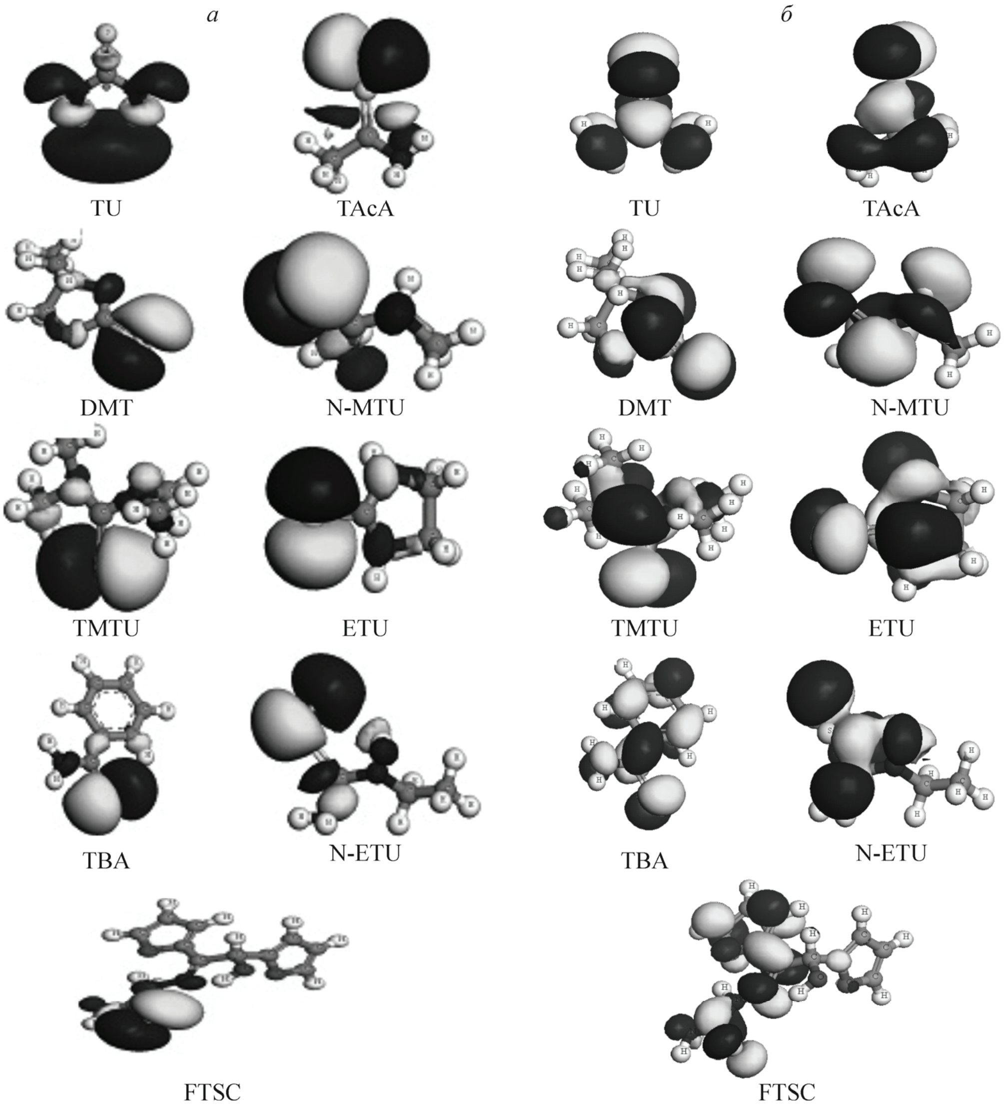

Fig. 7. Frontier molecule orbital density distributions of thio compounds: (*A*) HOMO and (*B*) LUMO

$$IE_{\text{Theo}}\% = -1.147E_{\text{H}} + 1.2E_{\text{L}} - 2.911\mu + 0.221C - 0.148E_{\text{H}}^2 + 0.307E_{\text{L}}^2 + \\ +0.641\mu^2 - 0.019C^2 + 2.47, \tag{3}$$

where E_{H} = HOMO, E_{L} = LUMO, μ = Dipole and C = concetration.

The frontier molecule orbital density distributions of thio compounds were also found (Fig. 7).

CONCLUSIONS

The correlation between the quantum chemical parameters and inhibition efficiencies of some thio compounds (contains a double-bond S atom) was investigated using DFT calculations. The inhibition efficiencies of the inhibitors are closely related to the quantum chemical parameters, HOMO, LUMO and dipole. The fact that inhibition efficiency is increased with increases in both E_{HOMO} and μ and decreases with E_{LUMO} is valuable. From the Fukui indices, it is found that the sites for nucleophilic and electrophilic attack are the sulfur atoms (S 18), (S 4), (S 8), (S 5), (S 6), (S 8), (S 6), (S 9) and (S 18) for the inhibitors (TU), (TAcA), (DMT), (N-MTU), (ETU), (TMTU), (N-ETU), (TBA) and (FTSC), respectively. QSAR approach was utilized in this study and a good relationship was found between $\text{IE}_{\text{exp}}\%$ and $\text{IE}_{\text{Theo}}\%$.The calculated inhibition efficiency was found closer to experimental inhibition with a coefficient of correlation (R^2) of 0.887.

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