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Theoretical studies on the efficiencies of some thio compounds as corrosion inhibitors of mild steel in HCl using PM6

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Abstract
Quantum chemical calculations were performed on 19 thio compounds using semi-empirical method PM6 within program package of Material Studio 5.5. The effect of molecular structure on the corrosion inhibition efficiency was investigated using the quantum chemical calculations. The electronic properties such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels, (LUMO – HOMO) energy gap, dipole moment (λ) and fraction of electron transfer (ΔN) were calculated and discussed.

Keywords: PM6, Corrosion Inhibition, Quantum Chemical Parameter

Introduction

Corrosion is the destructive attack of metal or alloy chemically or electrochemically against its environment which leads to 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 inhibitors are either synthesized from cheap raw materials or are chosen from organic compounds containing electronegative functional groups and pelectrons, triple or conjugated double bonds. The presence of heteroatoms (such as sulfur, oxygen, nitrogen) as well as aromatic rings in organic compounds facilitates the adsorption of the inhibitor on the metal surface in which the initial mechanism for the corrosion inhibition of the metal [2]. Some organic compounds are found to be effective corrosion inhibitors for many metals and alloys. It has been commonly recognized that organic inhibitor usually promotes formation of a chelate on the metal surface, which includes the transfer of electrons from the organic compounds to metal, forming coordinate covalent bond during such chemical adsorption process [3-5]. Some thio compounds are found to be good inhibitors for mild steel in acid [6-8]. Recently, theoretical chemical calculations have been used, such as quantum chemical calculations, to explain the mechanism of corrosion inhibition [9]. Quantum chemical calculations are proven to be a very powerful tool to understand the inhibition mechanism [10].

The present study is aimed to determine the relationships between molecular structures of 19 thio (sulfur) containing compounds namely: 6-thioguanine (TG) [5], 2,6-dithiopurine (DTP) [13], 4-amino-5-phenyl-4H-1, 2, 4-trizole-3-thiol (APTT) [6], N′-(3,4-dihydroxybenzylidene)-3-{[8-

(trifluoromethyl)quinolin-4-yl]thio}propanohydrazide (DHBTPH) [7], 3-{[8-(trifluoromethyl)quinolin-4-yl]thio}-N'-(2,3,4-trihydroxybenzylidene)propane hydrazide (TQTHBH) [8], 5-(1H-1,2,4-triazole-1-alkyl)-1,3,4-oxadiazole-2-thiol (TAOT) [9], N′-[4-(diethylamino)benzylidine]-3-{[8-(trifluoromethyl)quinolin-4-yl]thio}propane hydrazide) (DEQTPH) [10], Quinolin-5-ylmethylene-3-{[8-(trifluoromethyl)quinolin-4-yl]thio} propanohydrazide (QMQTPH) [11], 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole (4-MTHT) [12], N-(2-Thio benzimidazolyl methyl) isatin-3-isonicotinoyl hydrazone (TBIH) [13], thiourea (TU) [22], thioacetamide (TAcA) [22], 4,4-dimethyloxazolidine-2-thione (DMT) [23], N-methylthiocarbamide (N-MTU) [22], tetramethylthiocarbamide (TMTU) [22], 2-imidazolidinethione (ETU) [22], thiobenzamide (TBA) [22], N-ethylthiocarbamide (N-ETU) [22] and Schiff base furoin thiosemicarbazone (FTSC) [24] and their inhibition efficiencies. The selected thio compounds were previously reported as corrosion inhibitors for mild steel in 1.0 M HCl solution at 30°C. Through the method of quantum chemical calculations, the structural parameters, such as the frontier molecular orbital (MO) energy HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) and the fraction of electrons (ΔN) transfer from inhibitors to metal surface were calculated and correlated with corrosion inhibition efficiencies. The molecular structures for the selected thio compounds are shown in Figure 1.

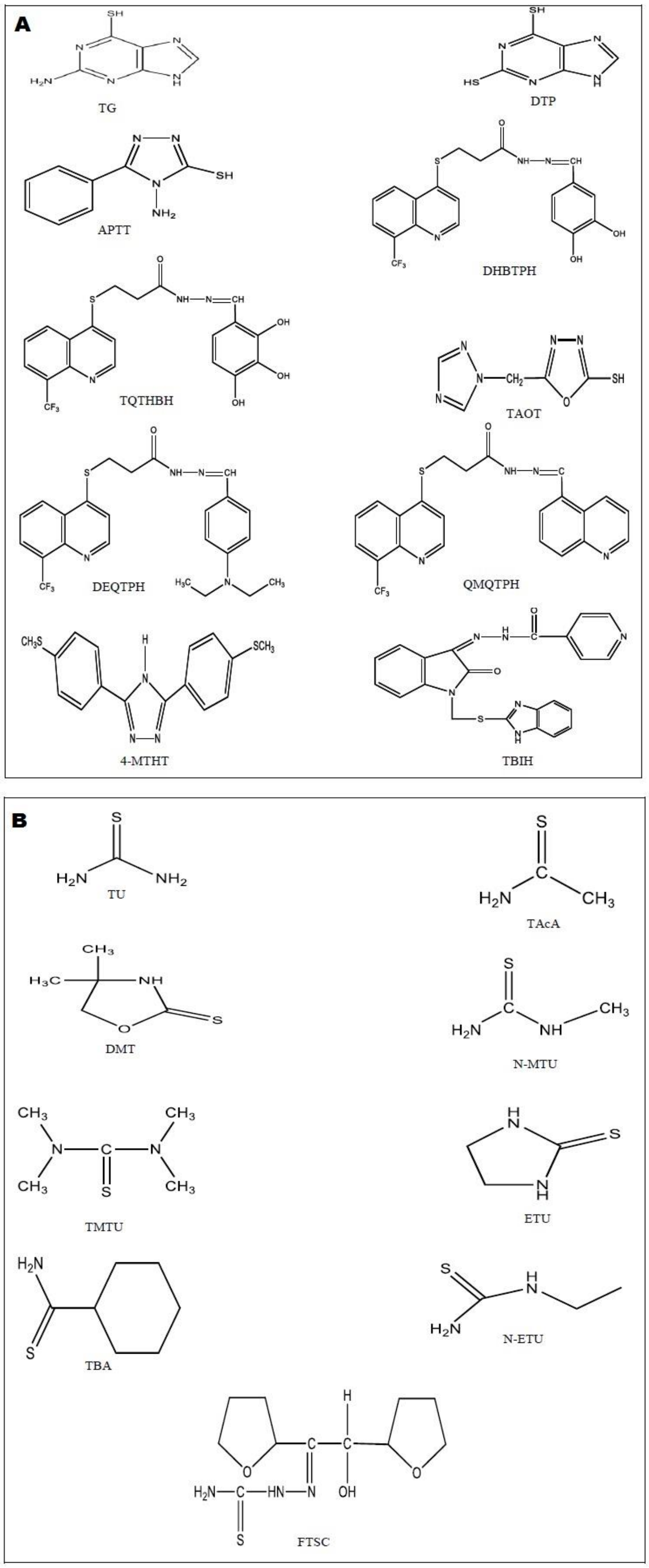

Fig.1. Molecular structure of studied molecules

Method of calculations

The quantum chemical calculations were performed using the VAMP 10.0 in Materials Studio 5.5 software. Parametric Method (PM6), semi-empirical method was employed to obtain the quantum chemical parameters and to optimize the molecule geometry. Complete geometry optimization of the molecules was carried out at ab initio level RHF (Restricted Hartree Fock theory) and SCF mode (self-consistent field). This basis set is known to provide accurate geometries and electronic properties for wide range of organic compounds. The optimization was repeated until minimum energy reached. 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 (λ), Mulliken atomic charges and number of transferred electrons (ΔN).

The numbers of transferred electrons (ΔN) were calculated based on the following quantum chemical method [15]:

$$\Delta N = \frac{(X_{Fe} - X_{inh})}{[2(\eta_{Fe} + \eta_{inh})]} \qquad (1)$$

Where X_{Fe} and X_{inh} denote the absolute electronegativity of mild steel and the inhibitor molecule, respectively; η_{Fe} and η_{inh} denote the absolute hardness of mild steel and the inhibitor molecule, respectively. These quantities are related to electron affinity (A) and ionization potential (I).

$$X_{inh} = \frac{I + A}{2} \qquad (2)$$

$$\eta_{inh} = \frac{I - A}{2} \qquad (3)$$

I and A are related in turn to E_{HOMO} and E_{LUMO} via

$$I = -E_{HOMO}$$

$$A = -E_{LUMO}$$

The fraction of electrons transferred (ΔN) from inhibitor to the mild steel molecule was also calculated using a theoretical X_{Fe} and η_{Fe}values for mild steel of 7 eV/mol and 0 eV/mol, respectively [16].

Results and Discussion

Quantum chemical calculations

The optimized molecule structure of the selected thio molecules are shown in Figure 2.

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

Frontier orbital theory is useful in predicting adsorption centers of the inhibitor molecules responsible for the interaction with surface metal atoms [17]. The terms involving the frontier molecular orbital could provide dominative contribution, because of the inverse dependence of stabilization energy on orbital energy difference. Studies by Fang and Li [3] have suggested that excellent corrosion inhibitors are usually those organic compounds which not only offer electrons to the unoccupied orbital of the metal but also accept the free electrons from the metal.

It can be seen from Table 1 that the obtained quantum chemical parameters changed irregularly with inhibition efficiency. The inhibition efficiency is misrelated with neither the changes of the E_{HOMO} and E_{LUMO}, which suggested that the inhibitors were perhaps neither the acceptor nor the donor of the electrons. This indicates there was no electron transferring in the interaction between the inhibitor molecules and the metal surface. Thus, the interactions are probably physical adsorption, and the interactions between the inhibitors and the metal surface might be ascribed to the hyper conjugation interactions-π stacking [18]. The frontier molecule orbital density distributions of thio compounds were presented in Figure 2.

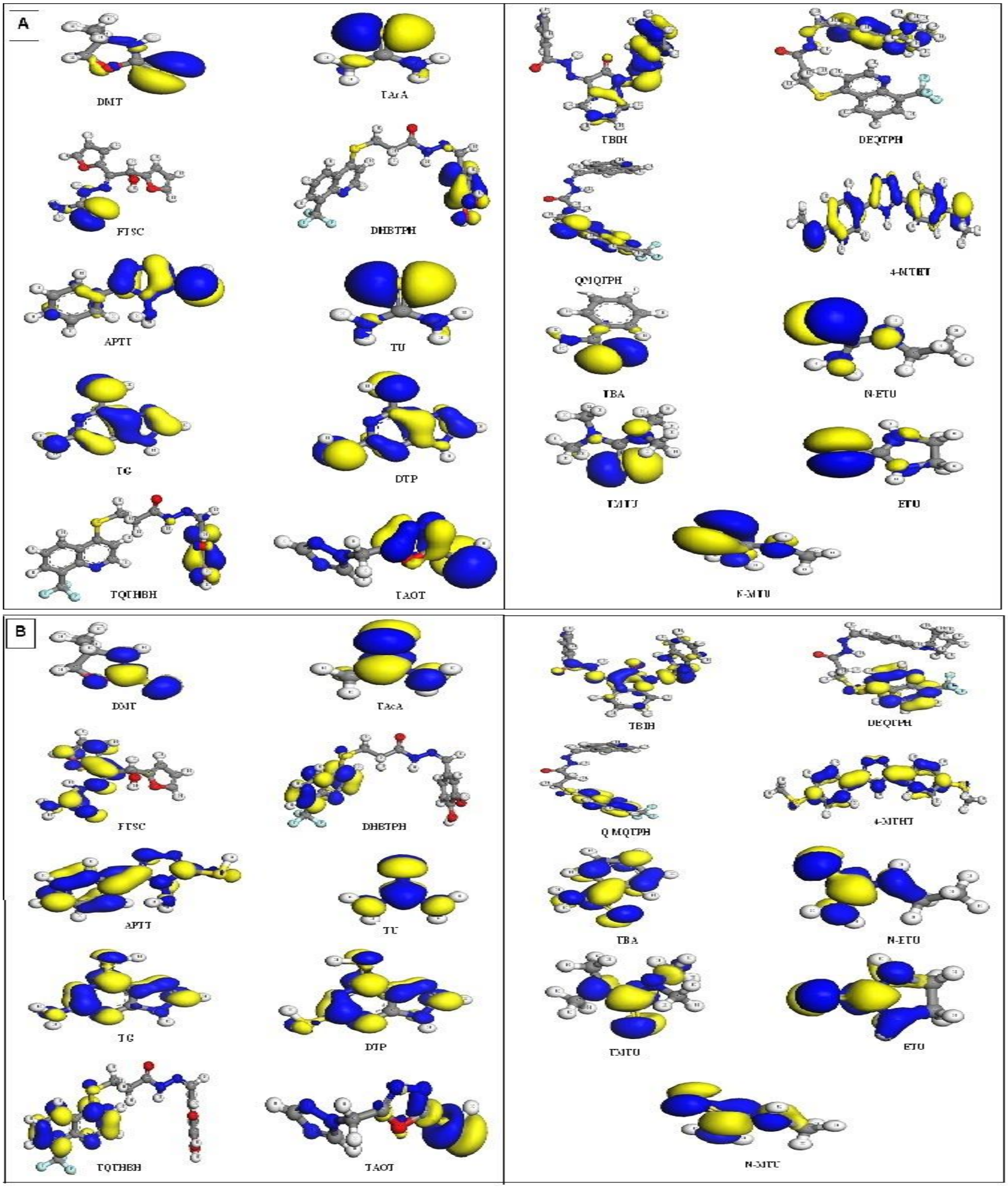

Fig. 2. The frontier molecule orbital density distributions of thio compounds: (**A**) HOMO and (**B**) LUMO.

As seen from the figure, the populations of the HOMO and LUMO focused around the sulfur and nitrogen atoms. The condition of physical adsorption is the presence of both electrically charged surface of the metal and charged species in the bulk of the solution; the presence of a metal having vacant low-energy electron orbital and of an inhibitor with molecules having relatively loosely bound electrons or heteroatom with lone pair electrons. Thus in the HCl acid medium, thio compounds may be protonated predominantly affecting the nitrogen atoms [18]. Thus, they become cations, existing in equilibrium with the corresponding molecular form. The protonated thio compounds, however, could be attached to the mild steel surface by means of electrostatic interaction between Cl- and protonated thio compound since the mild steel surface has positive charges in the acid medium [19]. This could further be explained based on the assumption that in the presence of Cl- would attach to positively charged surface. When thio compound adsorbs on the steel surface, electrostatic interaction takes place by partial transference of electrons from the polar atom (S and N atoms and the delocalized π electrons around the heterocyclic rings) of thio compound to the metal surface. In addition to electrostatic interaction (physisorption) of thio compound molecules on the mild steel surface, molecular adsorption may also play a role in the adsorption process. Thus the adsorption of thio compounds on the mild steel surface in HCl may be achieved by the interaction between iron atoms and heteroatom of sulfur. The electronic configuration of iron is [Ar]4s23d6, 3d orbital is not fully filled with electrons. The unfilled orbital of iron could bond with the highest occupied molecular orbital (HOMO) [20] of thio compound, while the filled 4s orbital of the former could interact with the lowest unoccupied molecular orbital (LUMO) of the latter.

Table 1. Molecular properties of the optimize thio compounds using PM6.

Compound	Inhibitor conc. (mM)	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{LUMO} - E_{HOMO}$ (eV)	λ	ΔN	IEexp%
TU	0.4	-8.69	0.234	-8.924	5.622	0.311	48.6
DMT	4	-8.726	0.164	-8.89	7.121	0.306	82.5
TBA	10	-8.686	-0.989	-7.697	4.779	0.281	97
N-ETU	10	-8.504	0.355	-8.859	6.43	0.330	95
TMTU	10	-8.282	0.181	-8.463	5.201	0.349	95
ETU	10	-8.601	0.179	-8.78	6.329	0.318	92
N-MTU	10	-8.541	0.342	-8.883	6.798	0.327	92
TAcA	10	-8.643	-0.126	-8.517	5.044	0.307	67
FTSC	3	-8.712	-1.002	-7.71	7.14	0.278	97.7
TG	1	-8.888	-0.778	-8.11	3.155	0.267	77.9
DTP	1	-9.063	-1.196	-7.867	1.524	0.238	85.9
TQTHBH	1.1	-9.332	-1.489	-7.843	2.851	0.203	88.9
TAOT	1	-9.967	-1.308	-8.659	4.085	0.157	89.1
TBIH	1.1	-9.187	-1.476	-7.711	1.062	0.216	98.04
QMQTPH	0.5	-9.337	-1.473	-7.864	4.312	0.203	93.1
APTT	0.4	-8.993	-0.683	-8.31	5.547	0.260	86.1
DHBTPH	1.15	-9.12	-1.477	-7.643	2.7	0.223	88.4
DEQTPH	1.05	-8.365	-1.542	-6.823	3.746	0.300	91.8
4-MTHT	0.5	-8.459	-0.883	-7.576	5.128	0.307	96.8

Mulliken charge and adsorption mechanism

The Mulliken charge distributions of the inhibitors are presented in Figure 3. It can be readily observed that sulphur, nitrogen atoms and the some carbons atoms have higher charge densities. The regions of highest electron density are generally the sites to which electrophiles attacked [34]. Therefore S, N and C atoms were the active centre, which have the strongest ability of bonding to the metal surface. On the other hand, HOMO (Figure 2A) was mainly distributed on the area containing sulphur and nitrogen atoms. Thus, this area is probably the primary site of the bonding. It was found that the studied inhibitors apart from existing in the cationic form which can interact with mild steel surface by electrostatic attraction. This interaction with the mild steel surface using a number of active centres is forming a good protective layer on the mild steel surface. The inhibition of acid corrosion by such organic cations is strongly influenced by the nature and charge of the metal surface.

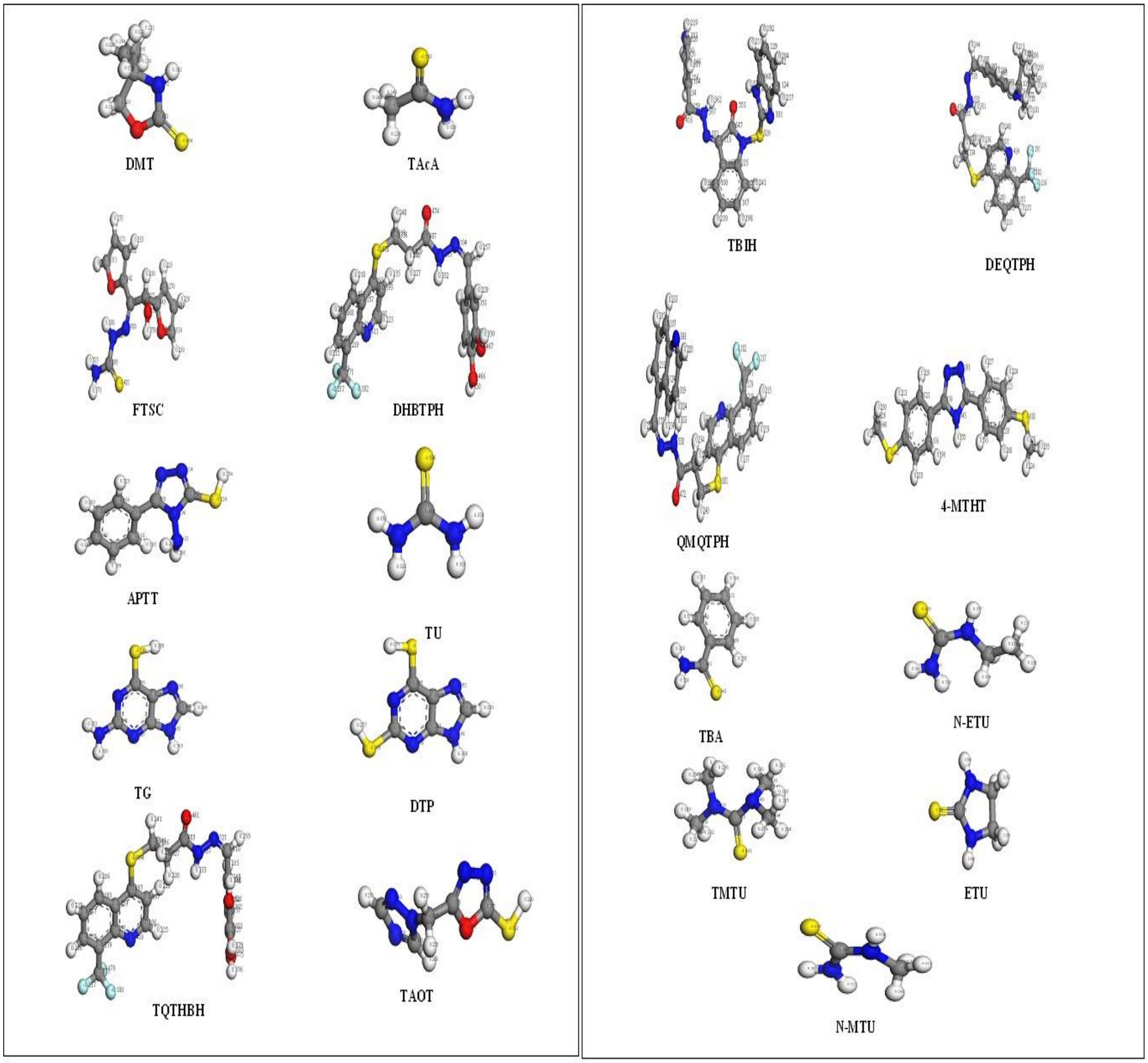

Fig. 3. Mulliken charges of thio molecules.

Conclusion

The relationships between inhibition efficiency of mild steel in 1M hydrochloric acid and the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap ($E_{LUMO} - E_{HOMO}$), dipole moment (λ), Mulliken atomic charges and number of transferred electrons (ΔN) of the thio compounds were calculated using the PM6-SCF method. Quantum chemical calculations have shown that apart from thio molecules adsorbing as cationic species on the mild steel surface, the adsorption of the molecule is take place through S atoms. The locations containing S and N atoms with high electron density is the most possible site for bonding the mild steel surface through electron donations to the metal surface.

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