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Theoretical determination of corrosion inhibitor activities of 4-allyl-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol-thione tautomerism

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Using the density functional method B3LYP/6-311G(d,p) calculations, the inhibitor activity of 4-allyl-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol tautomerism against corrosion of neutral copper surfaces has been investigated. Among the inhibitors tested, the 4-allyl-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol inhibitor has the inhibition performance for both forms (thiol and thione). Quantum chemical parameters that are correlated to the inhibition efficiency including highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital, (LUMO), energy bandgap (ΔE), electronegativity (χ), Hardness (η), softness (σ), dipole moment (μ), the fraction of the electrons transferred (ΔE), and Total energy (TE) has been calculated. In addition, the adsorption of inhibitors on the neutral copper surface reveals that nitrogen adsorption is preferred over sulfur adsorption. The results show that the thione form has the highest inhibitor compared to the thiol form.

Keyword: 1,2,3 Triazole, DFT, Corrosion Inhibitor Activity, Tautomerism

The use of organic coatings as a low-cost technique has long been known to avoid metal corrosion. By forming a film on the metal surface, organic inhibitors typically protect the metal from corrosion. As stated by several authors, their effectiveness is related to chemical composition, spatial molecular structure, molecular electronic structure, surface charge density, and metal surface affinity[1-6]. Also, due to the free electron pairs they possess, specific contact between functional groups and the metal surface and heteroatoms such as oxygen, nitrogen, sulfur, and phosphorus play an important role in inhibition. In recent years, organic inhibitors as cyclic aromatic compounds by delocalized pairs of π electrons in their multiple bonds have become one of the most used methods of corrosion control[7-9]. The azole family, especially 1,2,3 and 1,2,4-triazoles, are inhibitors corrosion process of metals such as copper, aluminum, and mild steel in various media[7,10-14].

In general, two mechanisms of organic substance inhibition activity have been proposed for the mild steel corrosion process; Adsorption of Inhibitor molecules at the active sites of the metal surface, displacing water molecules initially adsorbed at the same sites, and the development of a protective film involving the electrostatic attraction of the electrically charged metal surface between inhibiting ions (Inh^-) and dipoles (Fe^{2+} cations). In relation to the attraction between the metal and the water molecules, the maximum inhibition efficiency is due to the attraction forces between the Inh and the metal[15].

Other, quantum chemical studies have been conducted to obtain a better understanding of the interactions between the inhibitor molecule and the surface of the metal and to explain the defense mechanism against the corrosion phase[16-18]. Despite the number of experimental and computational studies that have been carried out to elucidate the organic anti-corrosion mechanism[7, 19]. Examples are triazole-type compounds comprising many heterocyclic structures that have excellent corrosion properties in different aggressive media for the corrosion of many metals[20].

The aim of this analysis is to explore the theoretical inhibitor corrosion properties of the title compound in a tautomerism form by quantum chemical calculation. The chemical structure of the compounds studied is as follows Fig. 1a.

Experimental Section

4-Allyl-5-pyridine-4-yl-4H-1,2,4-triazole-3-thiol synthesis was performed according to the method provided in the literature[21]. The synthesized molecular structure was analyzed by FT-IR, ^{1}H-NMR, and ^{13}C-NMR.

In a prevised study Experimentally used electrochemistry to determined inhibitor effects of 4-allyl-5-pyridin4-yl-4H-1,2,4-triazole-3-thiol on mild steel corrosion at room temperature in a 0.1 M H_2SO_4 solution. The derivative of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol-thione can be considered a strong mild steel corrosion inhibitor in the H_2SO_4 solution[22].

Computational methods

In the GaussView5.0 molecular imaging program, the approximate geometry of the molecules was plotted in the gas phase and the base case in three dimensions[23]. The GaussView 5.0 packet software was used to obtain the initial geometries of the molecules and measure them in the Gaussian09W software[24].

The DFT process, which takes into account the electron density and generates the desired data over this electron density, is used to improve the determination of the electronic properties of the structures, for a variety of reasons, B3LYP is a common option to use. It was one of the first methods that outperformed Hartree-Fock significantly[25-27]. B3LYP is typically quicker than most Post Hartree-Fock techniques and achieves comparable results. For a DFT technique, it is also fairly solid. It is not as highly parameterized as other hybrid functional on a more fundamental basis[28,29]. Besides, the Gaussian09W program provides the hybrid feature B3LYP, which is sufficient for the workstation's capability with 6-311G. (d,p) as a base set. Identifiers of electronic structures were determined from all geometry-optimized structures and E_{HOMO}, E_{LUMO}, ΔE, σ, χ, TE, μ and ΔN correlated with the behaviour of corrosion inhibition was investigated.

Results and Discussion

Experimental

Koparir *et al.* stated that the thiol crystal structure of compounds' corresponded to the form of thione, but they showed tautomerism of thiol-thione in solutions see Fig. 1b. Because of the thiol-thione tautomerism of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol it mostly appeared thiol form in solution[21].

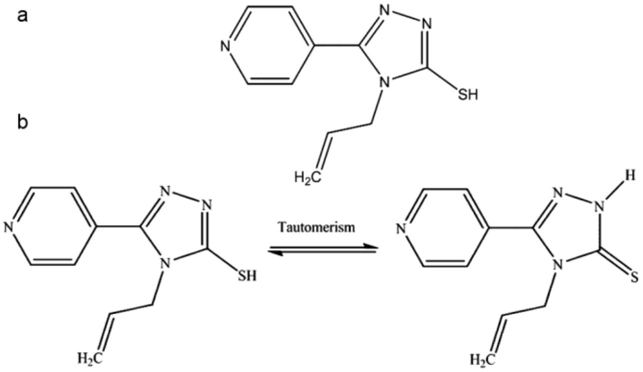

Fig. 1 — (a) 4-Allyl-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol; and (b) Thiole-thione tautomerism for title compounds

In a previous study we approved by cyclic voltammetry that two peaks were oxidation and observed for our title compounds, these peaks can be attributed to the oxidation of thiol groups. Also, the study was proved that 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol derivative can be regarded as a good inhibitor for mild steel corrosion in H_2SO_4 solution[22].

Theoretical Inhibitor activity

Using DFT (density functional theory) with Beck's three-parameter exchange functional along with the Lee-Yang-Parr nonlocal correlation functional, complete geometric optimizations of the investigated molecules are performed (B3LYP)[30-32] with the Gaussian 09 software bundle, the 6-311G (d,p) basis set is used. The adsorption centers of the inhibitor molecule can be predicted using frontier molecular orbitals (HOMO and LUMO). Adsorption should take place at the part of the molecule where the softness (σ) is a local property, has the highest value for the easiest transfer of electrons[33,34]. Koopman's theorem states that the energies of the inhibitor molecule's HOMO and LUMO orbitals are proportional to the ionization potential (*I*) and electron affinity (*A*) according to the following partnerships[35].

$$I = - E_{HOMO} \qquad \dots (1)$$

$$A = - E_{LUMO} \qquad \dots (2)$$

Electronegativity (χ), hardness (η), softness (σ) of the inhibitor molecule are given by the following relation

$$x = \frac{1}{2(I + A)} \qquad \dots (3)$$

$$= \frac{1}{2(I - A)} \qquad \ldots (4)$$

$$\sigma = \frac{1}{} \qquad \ldots (5)$$

The electrons transferred (ΔN) from the inhibitor to the Metal (Cu) atom are determined as follows using the values (χ and η) that have been determined theoretically.

$$\Delta N = \frac{xCu - xinh}{2(Cu - inh)} \qquad \ldots (6)$$

In the equation (6), the χ inhibitor and η inhibitor values are measured theoretically, while the χ metal and η metal values of the metal atom are determined experimentally by Pearson. According to Pearson η for single metal is taken as zero, and χ for cupper equal to eight. By optimizing bond lengths, bond angles, and dihedral angles, the geometric and electronic structures of the inhibitors can be determined. The optimized molecular structures with the lowest energies for both tautomerism molecules are shown in Fig. 2.

The geometrical structure for title compounds (Thiol-Thione) tautomerism shows the best positions for adsorption metal surface are S15-H25 for thiol and N12-H25 for thione. Calculations of the geometrical structure of the Thiol forme show that the bond length between S15–H25 a 1.347A^0 was higher compared with the bond length between N12-H25 in a thione form shown in Table 1, which can allow Thiol molecule adsorption on the metal surface through the sulfur atoms. The bond length for the 1,2,4-thiazole ring in a thiol form was smaller than the thion forme this is agreed with the expected above.

Mulliken population analysis is a commonly used tool for predicting the inhibitor molecules' adsorption

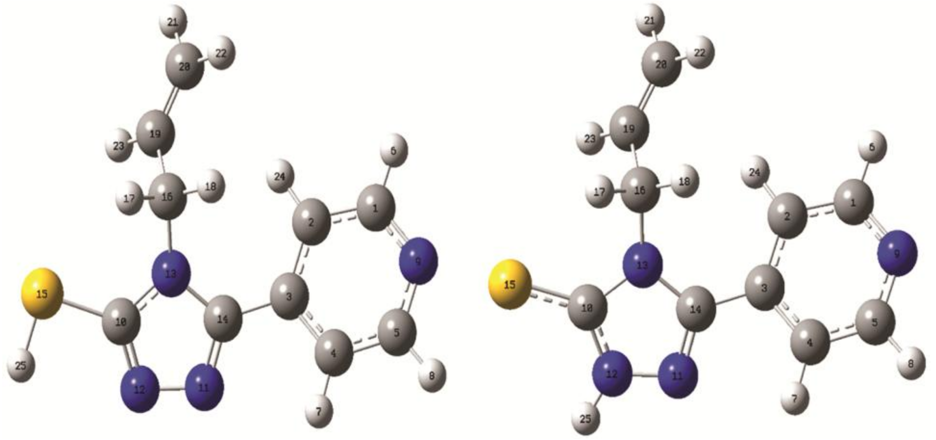

Fig. 2 — Tautomerism optimation structure calculated by B3LYP/ 6-311G (d,p)

Table 1 — Bond length for both molecules calculated by B3LYP/6-311G(d,p).

Thiol		Thione	
Symbol	Bond Length	Symbol	Bond Length
C2-C1	1.393	C2-C1	1.393
C3-C2	1.399	C3-C2	1.398
C4-C3	1.401	C4-C3	1.399
C5-C4	1.389	C5-C4	1.389
N9-C1	1.334	N9-C1	1.334
C10-C3	3.603	C10-C3	3.677
N11-C10	2.153	N11-C10	2.284
N12-C10	1.309	N12-C10	1.358
N13-C10	1.370	N13-C10	1.387
C14-N11	1.313	C14-N11	1.305
S15-C10	1.767	S15-C10	1.670
C16-N13	1.469	C16-N13	1.469
C19-C16	1.507	C19-C16	1.505
C20-C19	1.328	C20-C19	1.329
H25-S15	1.347	H25-N12	1.007

centers. The charge distribution on the atoms for both molecule's tautomerism is shown in Table 2. Many researchers agree that the existence of negatively charged heteroatoms enhances the ability of the molecule to adsorbs on metal surfaces via the donor-acceptor mechanism.

The negative charge on the nitrogen, sulfur, and carbons in the aromatic ringforthione form has an important inhibitory effect. Moreover, the negative charge on the Thiol atoms also was appeared except on the sulfur atoms, compared with thion atoms. View the molecular electrostatic potential map Fig. 3, the nitrogen atom of the triazole ring in a thiol form has denser red colour but is not a good potion for absorbed on the surface metal, while thione from the sulfur atom has a more negative value and attracted atom to absorb it.

E_{HOMO} is a quantum chemical descriptor that is often linked to a molecule's ability to donate electrons. A high E_{HOMO} value indicates that the molecule has a proclivity to donate electrons to a low-energy acceptor molecule. The molecule's ability to accept electrons is determined by the energy of the lowest unoccupied molecular orbital (E_{LUMO}). As a result, the lower E_{LUMO} is the more likely the molecule is to accept electrons[36].

With increasing HOMO and decreasing LUMO energy values, the inhibitor's ability to bind metal surfaces increases.The measurements indicate that thione form has the highest HOMO equal to -5.985 eV, with large coefficients localized on the sulfur and thiazol ring with very small coefficients on the ethylene group and pyridine ring Fig. 4, implying that the thione is most likely adsorbed on the copper surface through the sulfur and nitrogen atoms which has lone pair of electrons. As a result, its adsorption on the metal surface increases, and its inhibition efficiency rises. The lowest level of LUMO at thione form which is equal to -1.977 eV (Table 3), indicated the

Table 2 — Mulliken charge distribution on the atoms molecule.

Thiol		Thione	
Symbol	Charge distribution on the atoms	Symbol	Charge distribution on the atoms
C1	0.086	C1	0.095
C2	-0.161	C2	-0.163
C3	-0.028	C3	-0.032
C4	-0.126	C4	-0.122
C5	0.093	C5	0.072
N9	-0.305	N9	-0.317
C10	0.107	C10	0.087
N11	-0.224	N11	-0.236
N12	-0.202	N12	-0.225
N13	-0.349	N13	-0.348
C14	0.293	C14	0.312
S15	0.056	S15	-0.091
C16	-0.14	C16	-0.137
C19	-0.134	C19	-0.119
C20	-0.21	C20	-0.218

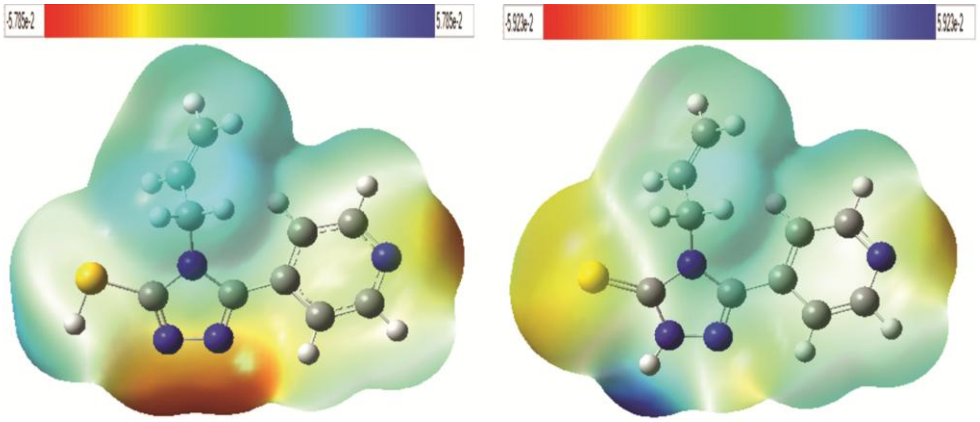

Fig. 3 — Molecular electrostatic potential map for thiol and thione molecule

Table 3 — Quantum chemical parameters calculation for the title compound

Parameters	Thiol	Thione
E_{LUMO} (eV)	-1.631	-1.977
E_{HOMO} (eV)	-6.535	-5.985
ΔE (eV)	4.903	4.007
χ (eV)	4.083	3.981
ɳ (Hardness)	2.451	2.003
σ (softness)	0.407	0.499
μ (Debye)	4.833	2.206
TE (eV)	-1004.398	-1004.425
ΔN	0.798	1.002

delocalization charge on the pyridine and ethylene groups Fig. 4. This explains why the thione molecule has the highest inhibition efficiency since the HOMO's energy is rising while the LUMO's energy is decreasing.

As a function of the inhibitor molecule's reactivity against adsorption on a metallic surface, the bandgap energy, ΔE = (E_{HOMO} - E_{LUMO}), is a significant parameter. The reactivity of the molecule increases as ΔE decreases and increasing the molecule's inhibition efficiency. According to the measurements, the thione molecule has the lowest ΔE value 4.007eV (Fig. 5 and

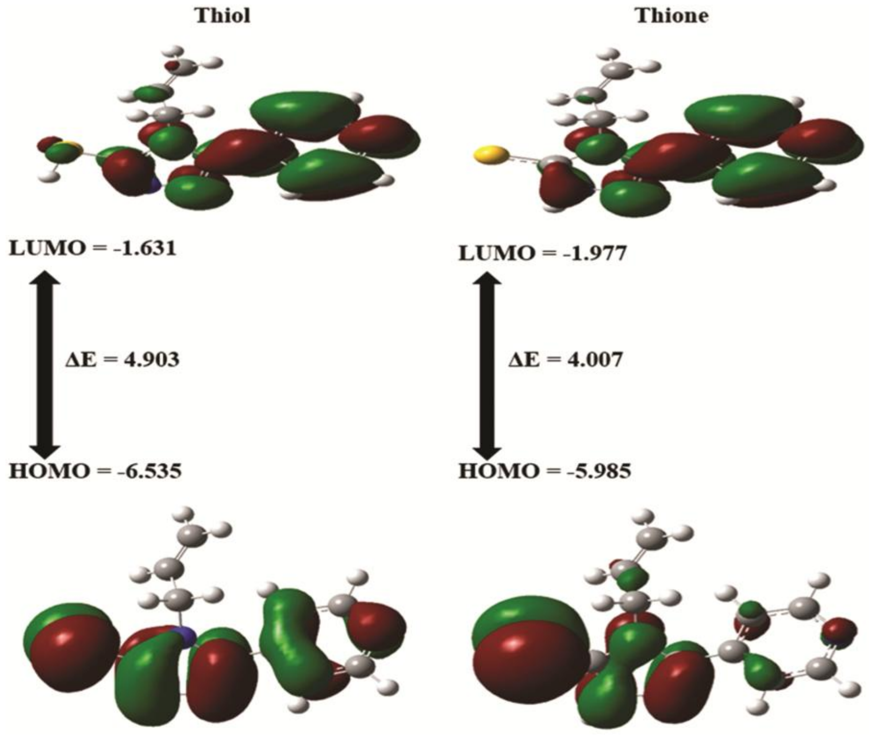

Fig. 4 — HOMO and LUMO delocalization charge on the atoms for both thiol and thione molecule inhibitors

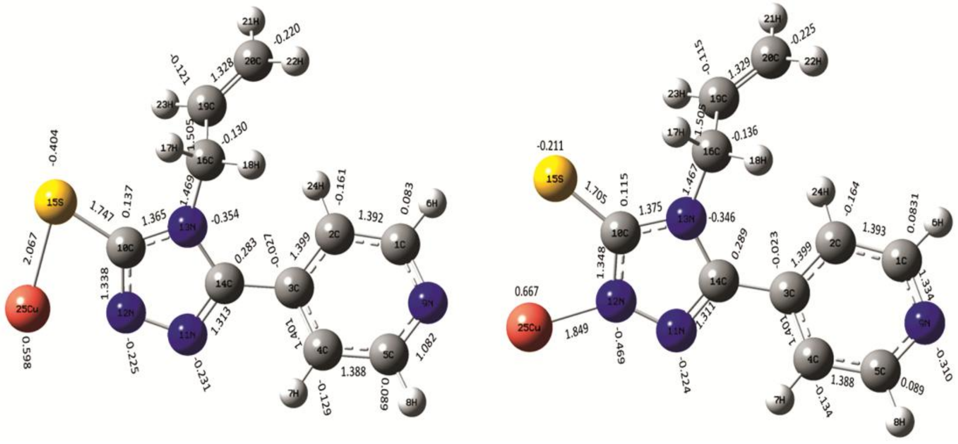

Fig. 5 — Cu–inhibitor complexes with optimized molecular structures

Table 3), which can help it adsorb on the metal surface and thus improve its inhibition performance.

The lower electronegativity value for inhibitors indicates that the copper metal can form a bond with the inhibitor compounds by taking electrons from it, allowing it to be better adsorbed to the metal surface and increasing the corrosion inhibition effect. Adsorption takes place in the softest region of the molecule. According to the calculations, thione has the highest softness on S atoms equal to 0.499, meaning that the sulfur atoms are responsible for the most thione adsorption on the metal surface.

The dipole moment is another parameter in Table 3. However, no direct correlation has been found in the literature between inhibition behaviour and dipole moment. According to some research, higher dipole moment value of molecules have better inhibition[33], whereas some literature said that lower dipole moment value of molecules have better inhibition[20]. The thione inhibitor has a low dipole moment, which is a better covering of the metal surface. Also, the total energy for thione forme has a little bit bigger than thiol forme, this is means thione forme has more inhibitor reactivity. The measured fraction of electrons transferred (ΔN) indicates that the thione molecule has more electrons transfer on the copper surface which is equal to 1.002e.

Adsorption Inhibitor on the metal surface

Organic inhibitor molecules are expected to produce their inhibition action by adsorbing to the metal surface. The molecular compositions of the inhibitors, the nature and charged surface of the metal, and the charge distribution over the whole inhibitor molecule, all have an impact on the adsorption mechanism. Two types of adsorption can be considered in general, the presence of an electrically charged metal surface and charged species in the bulk of the solution. Charge transfer or charge sharing from the inhibitor molecule to the metal surface is part of the chemisorption mechanism. This adsorption is aided by the presence of a transition metal with a low-energy vacant orbital and an inhibitor molecule with loosely bound electrons or a hetero atom with a lone pair of electrons. Figure 5 depicts to determined geometric and electronic structures of stable Cu–inhibitor complexes.

Calculations show that the Cu–thiol complex is formed when the inhibitor attacks the surface of the metal via S15, while the Cu–thione complex is formed via N12. As a result, the thione inhibitor is expected to adsorb intensely on the copper surface, while the thiol inhibitor is expected to adsorb weakly. According to the calculations, the Cu–S7 bond length in the case of the Cu–thiol is 2.067 A^0, while the bond length between Cu– N12 in a thione form is 1.849 A^0, this is approved that the thione form was strongly attached on the surface of the Cu. Also, an electron deficiency has affected the adsorption of the inhibitor on the metal surface, which found in Cu for thiol form equal to 0.598 while increased in a thione form this represents the thione form was more absorbed on the surface of the Cu.The quantum chemical parameters for Cu-inhibitor show in Table 4. In the case of the Cu-thione form, the energy bandgap (Fig. 6) was decreased compared with the Cu-thiol form, this approved that the stable complex was formed and the thione form was toughly attached to the Cu. Moreover, the increasing dipole moment of the Cu-thione represented the stability of the complex.

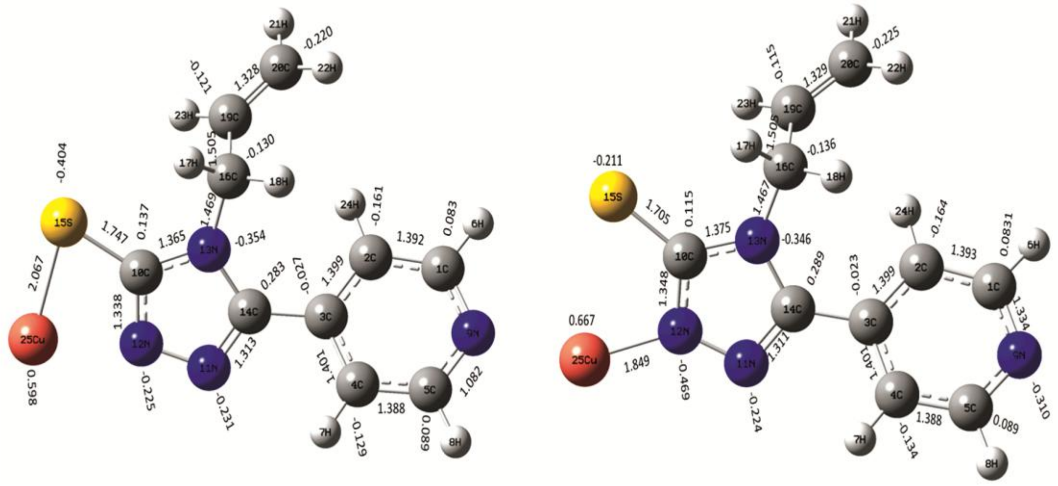

Fig. 6 — HOMO and LUMO Cu- complex for both thiol-thione tautomerism

Table 4 — Quantum chemical calculation for the Cu–inhibitor complexes

Parameters	Cu-Thiol	Cu-Thione
E_{LUMO}	-0.073	-0.092
E_{HOMO}	-0.192	-0.196
ΔE (eV)	0.118	0.104
μ (Debye)	2.631	3.324
TE (eV)	-2644.263	-2644.261

Conclusion

The inhibition efficiency of 4-allyl-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol tautomerism was successfully investigated using the DFT/B3LYP process. The HOMO and LUMO energies are correlated to the inhibition efficiency, according to the quantum parameters. A high E_{HOMO} value indicates that the inhibitor has a propensity to donate electrons to a suitable acceptor molecule, Cu surface, with a low empty molecular orbital energy. As a result, E_{LUMO}, the energy of the lowest unoccupied molecular orbital, shows the inhibitor molecule's ability to accept electrons, which means the lower the E_{LUMO} value, the greater the likelihood that the molecule will accept electrons. The inhibition efficiency improves as the HOMO energy values rise and the LUMO energy values fall. The inhibition efficiency of studied inhibitors is associated with the energy bandgap (ΔE), which is a function of reactivity. As ΔE decreases, the inhibitor's reactivity to the copper surface increases. A good correlation between inhibitor activity and softness, As the softness value, is increased, the inhibition efficiency improves. Bond length, Milliken charge distribution on atoms, and the molecular electrostatic potential map showed that the thione form has the highest inhibitor reactivity than thiol. Adsorption via the N atom in thione form is preferred over adsorption via the S atom in thiol form. Since it is adsorbed by the lone pair of electrons on the N atom and the pi charge on the ring, the thione inhibitor is the most efficient this matches the experimental findings very well.

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