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Characterization of Combined Adsorption using Fermi Levels, Molecular Dynamics, and Monte Carlo Simulations to Prevent Cu–Zn (111) Alloy Corrosion

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Abstract

Experimentally developing corrosion inhibitors requires a significant amount of money and time. In silico advancement empowers selecting inhibitor molecules based on their properties derived from theoretical studies, thereby reducing costs. Our main approaches include theoretical studies such as Fermi levels, electrostatic potential surface (EPS), Fukui indices, molecular dynamics stimulations, and Monte Carlo as indispensable tools to investigate the adsorption mechanisms of molecules 6-((5-(((3S,5R)-2-oxo-5-((2-(pyrazin-2-yloxy) thiazol-5-yl) thio) tetrahydro-2H-thiopyran-3-yl) oxy)isothiazol-3-yl)thio) nicotinic acid (PTT), and (S)-2-((5-(((3-(2-thioxoethoxy)-1,2,4-thiadiazol-5-yl)thio)-1,6-dihydropyrazin-2-yl)oxy)-1,3,4-thiadiazol-2-yl) thio) acetaldehyde (TTD) on the Cu/Zn (111) alloy. We electronically characterized PTT and TTD, which were proven effective inhibitors. Notably, all results suggested that the two exhibited high stability, enhanced reactivity, and strong surface adsorption, underscoring their potential use in practical applications. Such methodology may achieve high acceptance among scientists working on corrosion prevention. These properties are used to identify the mechanism of action of such blockers and ascertain their effectiveness. This comprehensive theoretical approach offers crucial insights for developing new and potent corrosion inhibitors, briefly explaining the reactivity concept between the molecules and the Cu/Zn surface.

Keywords: corrosion inhibitors, electronic characteristics, fermi energy, molecular dynamics, monte carlo

Introduction

Corrosion of metals is an electrochemical process, triggered by favorable environments such as acids and gases like CO₂ and SO₂ that damage surfaces; inhibitors are used to prevent it. Monte Carlo (MC) simulation is an important method for investigating the metal surface–inhibitor interaction. It can explain adsorption processes by identifying active sites on the inhibitor, where the most stable adsorption points with low energy are located [1, 2]. Molecules with multiple bonds, aromatic rings, delocalized π electrons, heteroatoms, or specific functional groups interact with the unoccupied surface d-orbitals, resulting in enhanced and effective corrosion inhibition. Such molecules can adsorb onto metal surfaces, blocking active sites and forming a protective barrier against corrosive agents [3, 4]. The simplest and most effective method for blocking copper (Cu)/zinc (Zn)-associated surface corrosion involves the chemisorption of molecules from aqueous solutions [5]. Theoretical studies are gaining importance in developing corrosion inhibitors by synthesizing new compounds with high efficacy [6]. Brass alloys, primarily composed of Cu and Zn with copper as the main component and zinc comprising 10% –

45% change color as the zinc content varies. A red color indicates pure copper, while yellow–white suggests a zinc content up to 45% [7]. Despite their considerable resistance to various corrosive media, these alloys remain susceptible under certain environments, leading to corrosion, cracking, and pitting. Copper/zinc alloys have attracted significant attention for their corrosion-resistant properties, making them extremely valuable in applications such as plumbing, heating, and cooling systems, household utensils, electrical fittings, and brass tubing used in manufacturing heat exchangers and coolers. Environments containing chloride, sulfate, or nitrate ions intensify Cu corrosion [8–10]. Bepotastine-B, an inhibitor for the corrosion of Cu–Zn alloys in cooling water, achieved an efficiency of 94.6% [11]. One of the most preferred methods to reduce corrosion and protect metals involves the use of compounds containing heteroatoms like 5-(4-methylpiperazin-1-yl)-1,3,5-dithiazinane and 6,13-dimethyl-3,10-dithia-1,5,8,12-tetraaza-tricyclo [10.2.2.10.2.2.25,8,8] octadecane [12]. This study evaluates new heterocyclic organic compounds as corrosion inhibitors. To lower production costs, the research focuses on analyzing and understanding the molecular properties of PTT and TTD. Such an analysis aims to aid in

developing effective inhibitors, investigate their performance, and clarify the fundamental mechanisms of Fermi energy and MC simulations that interpret surface adsorption onto a Cu/Zn alloy and its protection, making these blockers potentially suitable for practical use.

Methods

DFT and electronic characteristics methodology. Molecular dynamics (MD) simulations were performed to elucidate the adsorption of PTT and TTD onto the Cu–Zn (111) surface using the DMol3 module in Materials Studio; the COSMO Energy/EPS software was employed to investigate the inhibition mechanism. Exchange–correlation energy was treated with the Generalized Gradient Approximation parameterized with the Perdew–Burke–Ernzerhof functional and a Double Numerical Plus polarization basis set. To investigate dynamic behavior, simulations were conducted in the NVT ensemble at a constant temperature of 300 K, controlled by a Nose thermostat, for 1,000 steps with a time step of 1 fs. In MD simulations, only temperature but not pressure, was controlled. The molecular structures of PTT and TTD are shown in Figures 1 and 2. The electronic characteristics and molecular optimization, such as electrostatic potential surfaces (EPS), HOMO, and LUMO, were analyzed utilizing DMol3 [13]. Based on the E_{HOMO} and E_{LUMO} orbital energy values, electronegativity (χ) was calculated by applying equation 1 [14], softness (s) by equation 2 [15], hardness (η) by equation 3 [16], ionization energy (IE) by equation 4 [17], electron affinity (EA) by equation 5 [18], and energy gap (ΔE) by equation 6 [19].

$$\chi = \frac{-(E_{\text{HOMO}} + E_{\text{LUMO}})}{2} \quad (1)$$

$$s = \frac{1}{\eta} \quad (2)$$

$$\eta = \frac{\Delta E_{\text{gap}}}{2} \quad (3)$$

$$IE = -E_{\text{HOMO}} \quad (4)$$

$$EA = -E_{\text{LUMO}} \quad (5)$$

$$\Delta E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (6)$$

Fukui indices determine the nucleophilic, electrophilic, and radical sites depending on the electron transfer, as shown in equations 7, 8 [20], and 9 [21], where $q(N)$, $q(N + 1)$, and $q(N - 1)$ are the electronic populations of the atom k in neutral, anionic, and cationic systems, respectively. The second-order Fukui function Δf_k (condensed Fukui dual descriptor) was calculated using equation 10 [22].

$$f_k^+ = q_k(N + 1) - q_k(N) \quad \text{nucleophilic attack} \quad (7)$$

$$f_k^- = q_k(N) - q_k(N - 1) \quad \text{electrophilic attack} \quad (8)$$

$$f_k^o = \frac{1}{2} [q_k(N + 1) - q_k(N - 1)] \quad \text{radical attack} \quad (9)$$

$$\Delta f_k = f_k^+ - f_k^- \quad \text{condensed dual Fukui parameter} \quad (10)$$

Molecular dynamics foundations and monte carlo simulation. The quantum method predicts the ability of molecules to interact with metallic surfaces. MD and MC simulations are crucial and sensitive techniques for studying the metal surface–inhibitor interactions. MC simulations were performed at a size of $28.28 \text{ \AA} \times 28.28 \text{ \AA} \times 10.12 \text{ \AA}$ along with a $35 \text{ \AA}$ layer at the x -axis. The Cu/Zn crystallographic face, HKL111, was examined on the solid surface. Adsorption or interaction energy is the energy generated when one mole of the inhibitor is adsorbed on the metal surface (E_{ads}). When the adsorbed molecules cover the surface, the rigid energy E_{rigid} is released. The energy gained or released when the constituents are adsorbed on the metal surface is known as the distortion (deformation) energy (E_{def}) [23, 24]. Equation 11 defines the total energy as the sum of the deformation energy, stiff adsorption energy, and inhibitor molecules. The interaction between the molecules and the metal surface, as confirmed by the IE calculation, yielded MD data. It is pertinent to mention that the greater the IE negative value, the greater the binding affinity between inhibitors and the metal surface. Hence, the reciprocal of the adsorption energy equals binding energy (E_{bin}), as shown in Equation 12 [23].

$$E_{\text{Total}} = E_{\text{inhibitor molecules}} + E_{\text{rigid}} + E_{\text{deformation}} \quad (11)$$

$$E_{\text{Binding}} = -E_{\text{Interaction (adsorption)}} \quad (12)$$

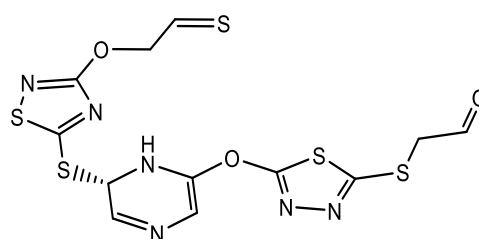


Figure 1. Schematic Structure of (S)-2-((5-((6-((3-(2-Thioxoethoxy)-1,2,4-Thiadiazol-5-yl)Thio)-1,6-Dihydropyrazin-2-yl)Oxy)-1,3,4-Thiadiazol-2-yl)Thio) Acetaldehyde (TTD)

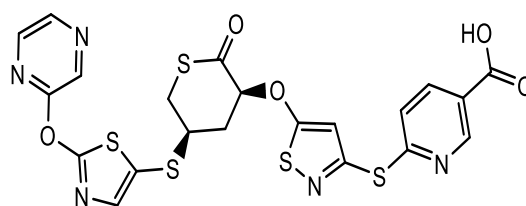


Figure 2. Schematic Structure of 6-((5-((3S,5R)-2-Oxo-5-((2-(Pyrazin-2-Yloxy)Thiazol-5-yl)Thio) Tetrahydro-2H Thiopyran-3-yl)Oxy) Isothiazol-3-yl)Thio)Nicotinic Acid (PTT)

Results and Discussion

HOMO, LUMO energies, and electronic characteristics. The energy values of the HOMO and LUMO orbitals are vital properties and closely interrelated; therefore, they should be interpreted. The PTT molecule results revealed the HOMO and LUMO values to be -5.414 eV and -3.376 eV, respectively; in contrast, those of the TTD molecule were -4.845 and -2.167 eV, respectively (Table 1). The E_{HOMO} values of PTT and TTD were high, whereas the E_{LUMO} values were low, confirming the efficiency of these inhibitors [25]. Figure 3 shows that electron density distributions in the HOMO and LUMO orbitals are characterized by inequality among molecules. These results indicate that PTT and TTD have active sites that can adsorb onto the Cu/Zn (111) surface, depending on the fact that HOMO is associated with the ability to donate electrons to PTT and DTT to accept electrons from the LUMO of the Cu/Zn (111) surface to be protected from corrosion. This observation was confirmed by the high E_{HOMO} energies, which indicate the tendency of the PTT and TTD molecules to donate electrons more quickly and facilitate adsorption to improve corrosion inhibition efficiency [26–28]. Furthermore, the electron density distribution of PTT and TTD was within the structure around a few sulfur and oxygen atoms and was concentrated minimally surrounding nitrogen atoms despite their presence at several sites. The low energy gap values of PTT and TTD molecules, 2.038 and 2.678 eV, respectively, and low hardness values, 1.019 and 1.339 eV, respectively, indicate enhanced reactivity and facilitate adsorption onto the Cu/Zn (111) surface, elevating inhibition performance. The decrease in each LUMO and energy gap with an increase in HOMO energy implies an enhancement in PTT and TTD efficiency. IE and electron affinity describe the electron-donating and -accepting abilities of the PTT and TTD molecules, respectively. Electron donation is enhanced as the ionization potential decreases. The IE of PTT is larger than that of TTD; therefore, the TTD molecule is best in electron donation [25, 29]. MD-TTD is the molecular dynamics of the compound (S)-2-((5-((6-((3-(2-thioxoethoxy)-1,2,4-thiadiazol-5-yl)thio)-1,6-dihydropyrazin-2-yl)oxy)-1,3,4-thiadiazol-2-yl)thio) acetaldehyde, while MD-PTT is the dynamics of 6-((5-((3S,5R)-2-oxo-5-((2-(pyrazin-2-yloxy)thiazol-5-yl)thio)tetrahydro-2H-thiopyran-3-yl)oxy)isothiazol-3-yl)thio) nicotinic acid.

Electrostatic Potential Surface (EPS). EPS is a vital characteristic that must be considered while determining the reaction-related areas of the molecules. It is crucial for determining molecule dimensions, form, and capacity as well as to simultaneously use color grading. The red areas are more negative regions, while the blue areas are more positive sites, indicating electrophilic and nucleophilic reactions. The green, pink, and pale yellow regions represent a mix of the two hues blue and red, which are

electrophilic and nucleophilic simultaneously (Figure 4). The EPS distribution map explains that oxygen 7 ; 23 sulfur12; and nitrogen 3, 9, and 10 atoms of the TTD inhibitor act as local nucleophilic best centers *via* adsorption onto the Cu/Zn (111) surface, while the H₂₇, C₂₀, C₂₅, and H₃₄ atoms act as local electrophilic best centers. Regarding PTT molecules, the oxygen 34; sulfur 12 and 19; and nitrogen 10 and 17 atoms act as local nucleophilic best centers during adsorption onto Cu/Zn (111). In contrast, the H₄₃, C₂, C₉, and C₃₃ atoms act as the best electrophilic centers within the local area. The EPS values and fitting point charges on all atoms are shown in Tables 2 and 3. The TTD molecule showed negative potential values for atoms of O₇ (-0.722 e), O₂₃ (-0.593 e), S₁₂ (-0.734 e), N₃ (-0.332), N₉ (-0.586), and N₁₀ (-0.811); positive values for hydrogen and carbon atoms; and with high values for C₂₀ (0.547 e), C₂₅ (0.424 e), H₂₇ (0.525 e), and H₃₄ (0.738 e). Furthermore, the PTT molecule showed negative values for atoms of O₃₄ (-0.812 e), S₁₂ (-0.321 e), S₁₉ (-0.603 e), N₁₀ (-0.306 e), and N₁₇ (-0.448 e); however, the hydrogen and carbon atoms showed positive values, in particular high values for C₂ (0.647 e), C₉ (0.444 e), C₃₃ (0.327 e), and H₄₃ (0.695 e). The large region of yellow and pink surroundings indicates a low electrostatic potential focus (Figure 4). Electrophilic attack was indicated by the red negative region encompassing most sulfur, nitrogen, and oxygen atoms. Consequently, through EPS analysis, the reactive zones of PTT and TTD were systematically evaluated, and varied hue grades made it easier to understand the mechanisms by which molecules are adsorbed on the Cu/Zn surface [29–31].

Fukui index and fermi level. The Fukui indices describe the active sites of the molecules that possibly adapt to electrophilic and nucleophilic attacks. Large f_k^+ and f_k^- values indicate molecule softness and chemically reactive sites. A high f_k^+ at a site signifies pronounced electrophilic properties, i.e., it is vulnerable to nucleophilic attacks. A high f_k^- suggests nucleophilic characteristics and is susceptible to electrophilic attacks. The Δf_k is more explicit and accurate than f_k^+ or f_k^- in determining active sites; it assesses sites that are concurrently nucleophilic and electrophilic.

Table 1. Electronic Characteristics of PTT and TTD Ascertained by the DMol3 Software

Quantum Chemical	PTT (eV)	TTD (eV)
HOMO	-5.414	-4.845
LUMO	-3.376	-2.167
Energy gap (E_{gap})	2.038	2.678
Electronegativity (χ)	4.395	3.506
Softness (s)	0.981	0.746
Hardness (η)	1.019	1.339
Ionization energy (IE)	5.414	4.845
Electron affinity (EA)	3.376	2.167

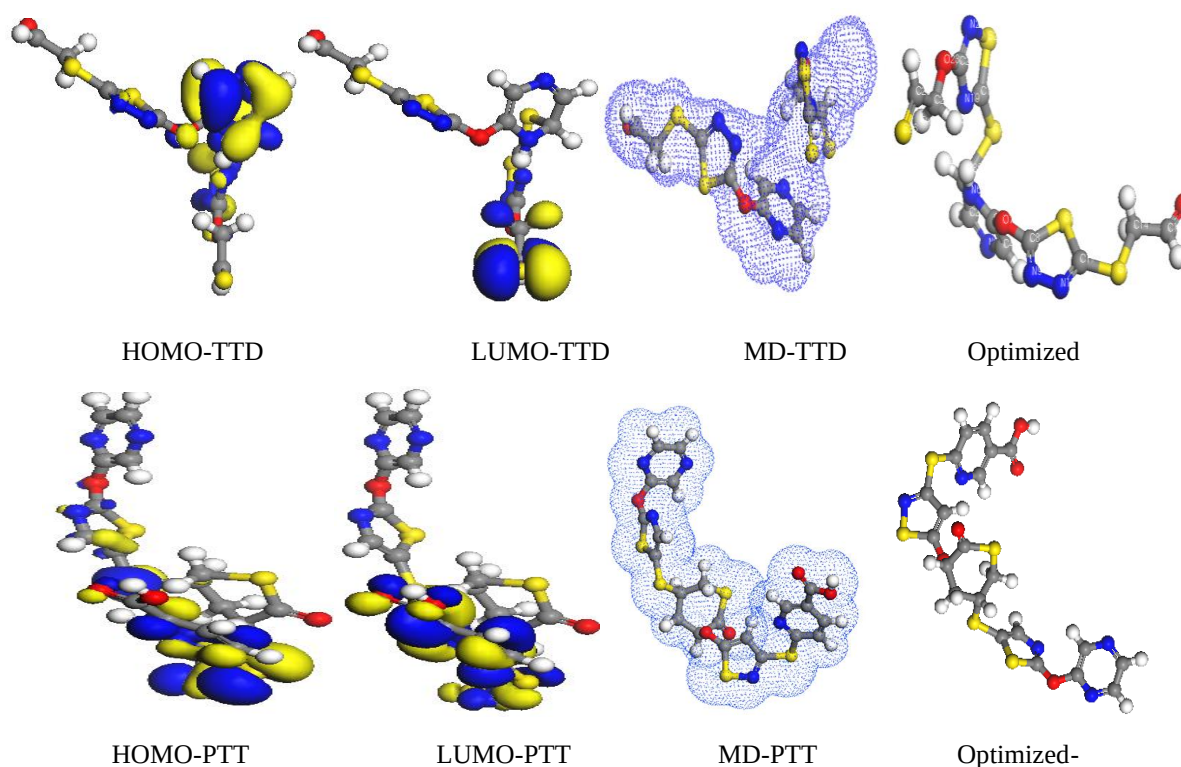


Figure 3. HOMO, LUMO, MD, and Optimal TTD and PTT Molecules

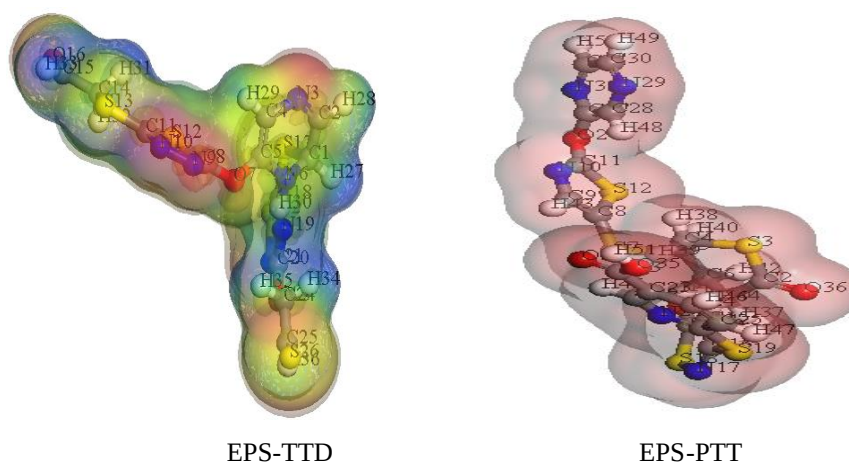


Figure 4. Electrostatic Potential Map of the PTT and TTD Molecules

The atoms that possess positive and negative Δf_k values are preferred for electrophilic and nucleophilic attacks, respectively [29, 32, 33]. Table 4 shows the f_k^+ , f_k^- , and Δf_k of the PTT and TTD molecules. The C₂, C₂₀, C₂₅, H₂₇, H₃₁, H₃₂, and H₃₄ atoms of the TTD molecule exhibited the maximum f_k^+ , indicating them to be active sites of nucleophilic attacks. In contrast, O₇, O₂₃, S₁₂, N₃, N₉, N₁₀, and N₂₁ demonstrated the greatest f_k^- , suggesting that they are reactive sites for electrophilic attacks. The N₁₇, N₂₁, O₃₄, S₇, S₁₂, and S₁₉ atoms of the PTT inhibitor exhibited the highest f_k^- , elucidating that they are active sites for electrophilic attacks. In contrast, C₂, C₉, C₃₃, H₃₈, and

H₄₃ revealed the maximum f_k^+ , indicating they are the reactive sites for nucleophilic attacks. However, the atoms that possess a positive Δf_k value prefer electrophilic attacks against the Cu/Zn (111) surface, indicative of their robust electron-accepting ability when interacting with the metal surface, while the atoms that possess a negative value choose nucleophilic attacks (Table 4). In essence, nucleophilic sites are located at the heteroatoms; in contrast, the carbon and hydrogen atoms mainly behave as electrophilic centers available for bonding with the Cu/Zn (111) surface.

Table 2. Fitting Point Charges and EPS Results V(R) on All Atoms of the PTT

Atoms	Charge (e)	V(r) (a.u)	Atoms	Charge (e)	V(r) (a.u)	Atoms	Charge (e)	V(r) (a.u)
C (1)	0.002	-1.1241	S (18)	-0.171	-1.0914	O (35)	-0.022	-12.756
C (2)	0.647	-1.0929	S (19)	-0.603	-2.0786	O (36)	-0.014	-9.7557
S (3)	-0.040	-1.9914	C (20)	0.164	-1.1171	H (37)	0.012	-9.7698
C (4)	0.011	-1.9761	N (21)	-0.142	-2.0991	H (38)	0.023	-9.7186
C (5)	0.015	-1.9910	C (22)	0.112	-2.1177	H (39)	0.115	-9.6953
C (6)	0.004	-1.9990	C (23)	0.022	-2.1171	H (40)	0.115	-9.7225
S (7)	-0.002	-1.1906	C (24)	0.020	-5.1124	H (41)	0.014	-22.394
C (8)	0.012	-2.9808	C (25)	0.026	-5.1193	H (42)	0.019	-22.301
C (9)	0.444	-2.2352	O (26)	-0.227	-17.344	H (43)	0.695	-22.359
N(10)	-0.306	-2.7632	C (27)	0.028	-17.333	H (44)	0.007	-22.110
C (11)	0.005	-3.1192	C (28)	0.051	-21.312	H (45)	0.097	-14.001
S (12)	-0.321	-3.1107	N (29)	-0.112	-21.391	H (46)	0.115	-22.728
O (13)	-0.020	-2.1132	C (30)	0.022	-12.723	H (47)	0.115	-22.856
C (14)	0.004	-2.1043	C (31)	0.020	-14.762	H (48)	0.014	-32.753
C (15)	0.007	-0.9539	N (32)	-0.026	-14.728	H (49)	0.119	-32.692
C (16)	0.038	-1.7291	C (33)	0.327	-14.324	H (50)	0.124	-32.732
N (17)	-0.448	-1.0954	O(34)	-0.812	-14.190	H (51)	0.092	-32.501

Table 3. Fitting Point Charges and EPS Results V(R) on All Atoms of The TTD

Atoms	Charge (e)	V(r) (a.u)	Atoms	Charge (e)	V(r) (a.u)	Atoms	Charge (e)	V(r) (a.u)
C (1)	0.137	-20.304	S (13)	0.164	-8.7186	C (25)	0.424	-18.721
C (2)	0.144	-22.315	C (14)	0.142	-18.655	S (26)	-0.123	-1.0296
N (3)	-0.332	-16.315	C (15)	0.116	-11.757	H (27)	0.525	-1.0304
C (4)	0.118	-12.307	O (16)	-0.127	-29.344	H (28)	0.089	-1.9761
C (5)	0.078	-15.752	S (17)	-0.172	-13.231	H (29)	0.165	-3.1179
N (6)	-0.227	-16.762	C (18)	0.285	-13.354	H (30)	0.219	-5.0991
O (7)	-0.722	-16.756	N (19)	-0.134	-12.374	H (31)	0.221	-5.1160
C (8)	0.202	-16.783	C (20)	0.547	-18.727	H (32)	0.192	-5.1170
N (9)	-0.586	-18.622	N (21)	-0.102	-12.728	H (33)	0.163	-7.1252
N(10)	-0.811	-17.756	S (22)	-0.092	-14.705	H (34)	0.738	-8.1132
C(11)	0.171	-14.755	O (23)	-0.593	-14.713	H (35)	0.121	-2.7692
S(12)	-0.734	-18.769	C (24)	0.189	-14.422	H (36)	0.156	-12.322

The molecules possess several effective centers that enhance their adsorption onto the Cu/Zn surface to elevate inhibition [29]. The Fukui index and the adsorption geometries suggest that this process was supported primarily through heteroatoms. Most atoms of both molecules possess high electrophilicity and nucleophilicity, providing additional reactive sites that could enhance the affinity of PTT and TTD molecules toward Cu and Zn atoms. The Fermi level has very functional relevance in the interpretation of adsorption, where the HOMO energies of the PTT and TTD molecules were -5.414 and -4.845 eV, respectively, which were higher than the Fermi energy of Cu/Zn at -7.22 eV. Furthermore, they were significantly greater than the Fermi energies of the PTT and TTD molecules, -23.12 and -23.93 eV (-0.88 Ha), respectively

(Figures 5, 6, and 7), confirming their enhanced adsorption ability onto the copper/zinc surface. The region around -7.22 eV was close to the Fermi level of Cu/Zn; it has a higher density than other regions and supports charge transfer from PTT and TTD molecules to the Cu/Zn (111) [30]. Additionally, a band did not surpass the Fermi level; it was noted that the minimum conduction and the maximum valence bands did not overlap; therefore, metallic features appeared [34].

MD and MC simulations. Understanding the adsorption of molecules on metals is difficult since the molecules can attach in different forms depending on the metal surface and the active centers of the molecules.

Table 4. Evaluation of the Fukui Functions and Dual-Descriptors of PTT and TTD using the Dmol3 Software (Maximum Value in Bold)

PTT Molecule					TTD Molecule				
Atoms	f_k^+	f_k^-	f_k^0	Δf_k	Atoms	f_k^+	f_k^-	f_k^0	Δf_k
C(1)	0.001	-0.002	-0.001	0.003	C(1)	-0.002	-0.025	-0.012	0.023
C(2)	0.313	0.000	0.006	0.313	C(2)	0.204	0.054	0.029	0.150
S(3)	0.013	0.020	0.031	-0.007	N(3)	0.005	0.284	0.018	-0.279
C(4)	-0.003	-0.011	-0.007	0.008	C(4)	0.004	0.076	0.039	-0.072
C(5)	-0.003	-0.015	-0.009	0.012	C(5)	0.003	0.035	0.017	-0.032
C(6)	-0.002	-0.004	-0.003	0.002	N(6)	0.003	0.004	0.022	-0.001
S(7)	0.012	0.173	0.092	-0.161	O(7)	0.001	0.119	0.011	-0.118
C(8)	0.003	-0.004	-0.001	0.007	C(8)	0.000	-0.011	-0.010	-0.011
C(9)	0.099	0.032	0.019	0.067	N(9)	0.002	0.124	0.008	-0.122
N(10)	0.005	0.022	0.013	-0.017	N(10)	0.001	0.311	0.006	-0.210
C(11)	0.000	0.020	0.010	-0.020	C(11)	0.001	0.004	0.003	-0.003
S(12)	0.020	0.153	0.036	-0.133	S(12)	0.003	0.199	0.009	-0.196
O(13)	0.004	0.006	0.005	-0.002	S(13)	0.003	0.019	0.011	-0.016
C(14)	0.007	0.006	0.006	0.001	C(14)	-0.001	-0.002	-0.002	0.001
C(15)	0.003	0.012	0.008	-0.009	C(15)	0.006	0.001	0.004	0.005
C(16)	0.001	-0.001	0.000	0.002	O(16)	0.005	0.191	0.003	-0.186
N(17)	0.019	0.124	0.021	-0.105	S(17)	0.014	0.131	0.071	-0.117
S(18)	0.036	0.067	0.051	-0.031	C(18)	0.004	0.002	0.006	0.002
S(19)	0.061	0.162	0.112	-0.101	N(19)	-0.005	0.009	0.001	-0.014
C(20)	0.044	0.001	0.022	0.043	C(20)	0.108	0.022	0.015	0.086
N(21)	0.021	0.220	0.020	-0.199	N(21)	0.010	0.198	0.024	-0.188
C(22)	0.035	0.017	0.026	0.018	S(22)	0.022	0.016	0.048	0.006
C(23)	0.028	0.026	0.027	0.002	O(23)	0.006	0.116	0.011	-0.010
C(24)	0.043	0.013	0.028	0.030	C(24)	-0.024	-0.006	-0.016	-0.018
C(25)	0.018	0.027	0.022	-0.009	C(25)	0.208	0.018	0.114	0.190
O(26)	0.009	0.013	0.011	-0.004	S(26)	0.068	0.003	0.337	0.065
C(27)	0.025	0.005	0.015	0.020	H(27)	0.203	0.034	0.019	0.169
C(28)	0.039	0.007	0.023	0.032	H(28)	0.003	0.033	0.018	-0.030
N(29)	0.052	-0.012	0.032	0.064	H(29)	0.003	0.038	0.020	-0.035
C(30)	0.025	0.009	0.017	0.016	H(30)	0.000	0.019	0.009	-0.019
C(31)	0.038	0.006	0.022	0.032	H(31)	0.202	0.003	0.002	0.199
N(32)	0.050	0.011	0.031	0.039	H(32)	0.112	0.003	0.002	0.109
C(33)	0.360	0.011	0.036	0.349	H(33)	0.002	0.002	0.002	0.000
O(34)	0.007	0.318	0.037	-0.311	H(34)	0.194	0.021	0.048	0.173
O(35)	0.027	0.007	0.017	0.020	H(35)	0.072	0.021	0.047	0.051
O(36)	0.019	0.019	0.019	0.000	H(36)	0.093	0.032	0.063	0.061
H(37)	0.008	0.012	0.010	-0.004					
H(38)	0.324	0.002	0.008	0.322					
H(39)	0.004	0.015	0.009	-0.011					
H(40)	0.004	0.022	0.013	-0.018					
H(41)	0.006	0.014	0.010	-0.008					
H(42)	0.005	0.012	0.009	-0.007					
H(43)	0.115	0.023	0.014	0.092					
H(44)	0.009	0.015	0.012	-0.006					
H(45)	0.025	0.015	0.020	0.010					
H(46)	0.027	0.014	0.021	0.013					
H(47)	0.023	0.019	0.021	0.004					
H(48)	0.022	0.007	0.015	0.015					
H(49)	0.022	0.047	0.015	-0.025					
H(50)	0.023	0.077	0.015	-0.054					
H(51)	0.016	0.096	0.011	-0.080					

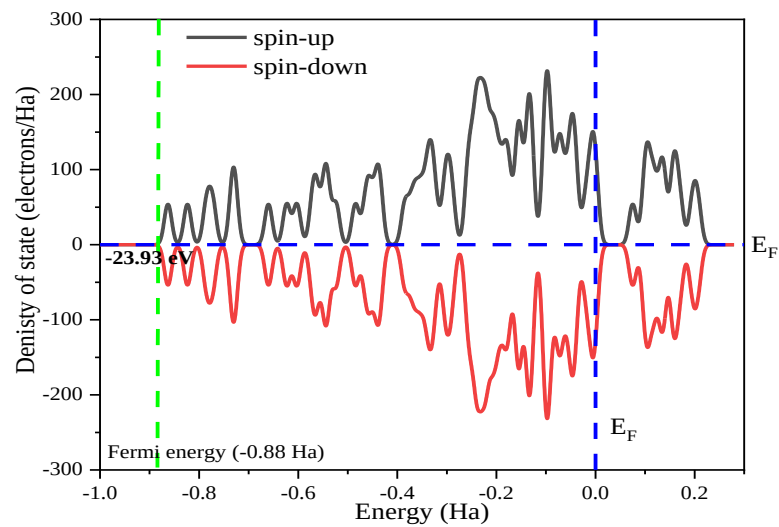


Figure 5. Fermi Energy of the TTD Molecule Ascertained by the DMol3 Software

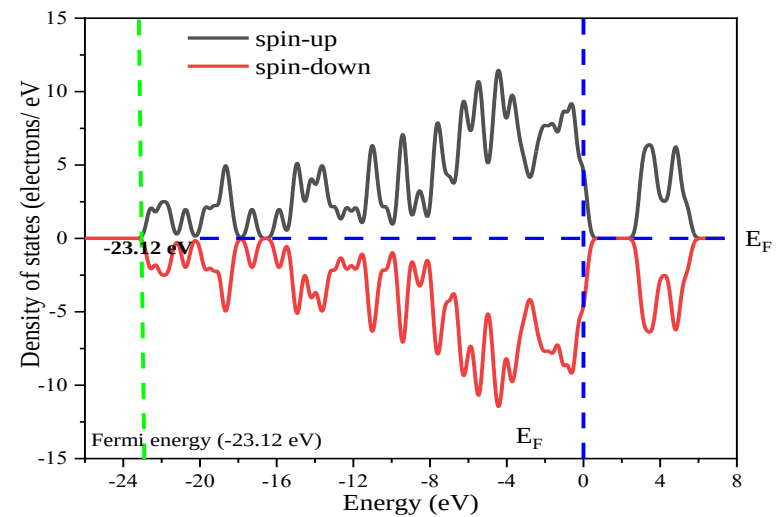


Figure 6. Fermi Energy of the PTT Molecule Assessed by the DMol3 Software

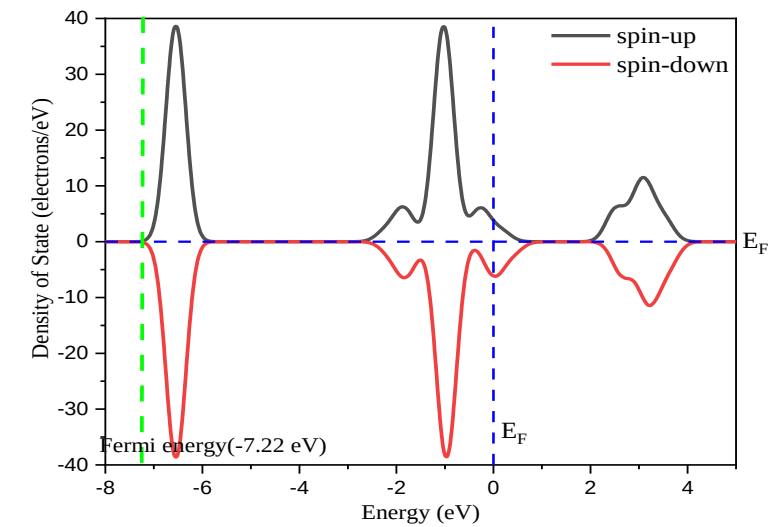
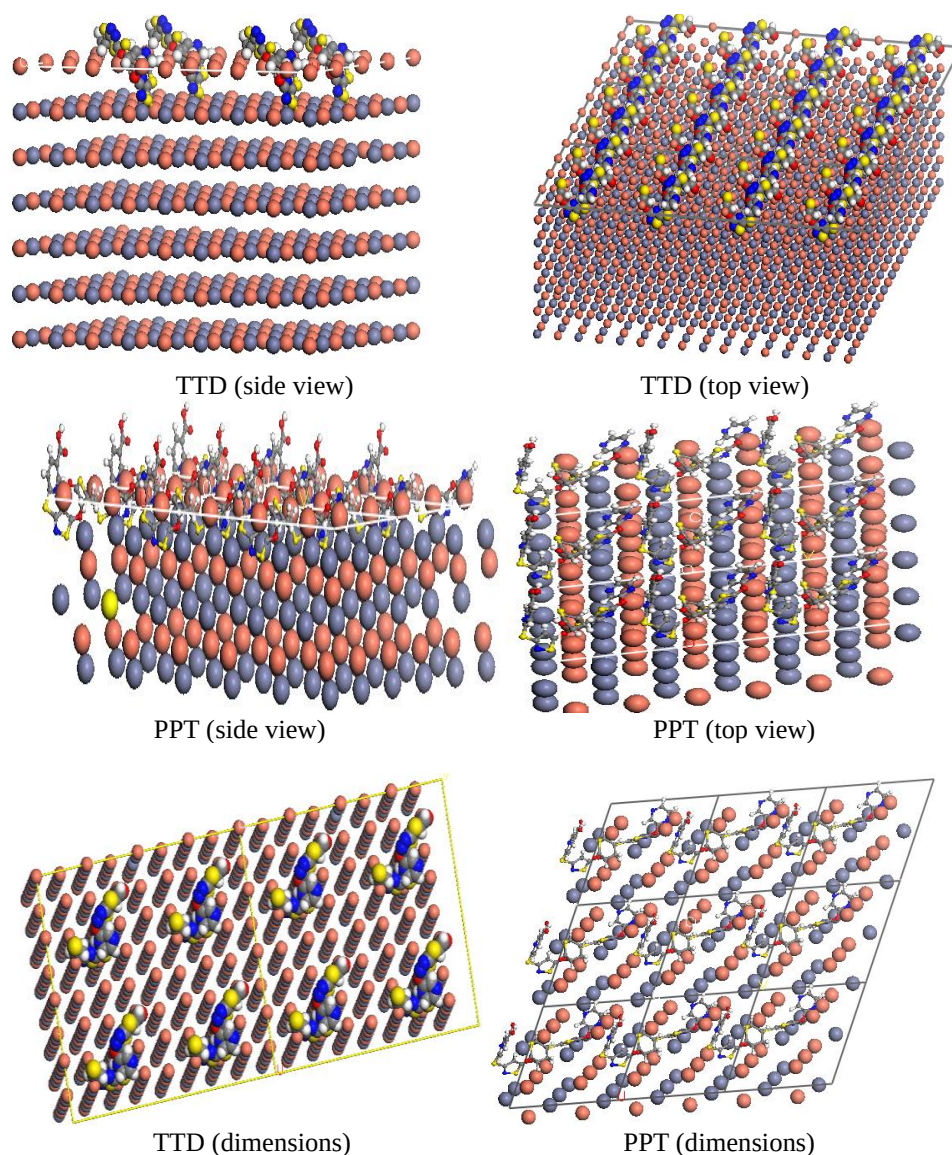


Figure 7. Fermi Energy of Cu/Zn Alloy Determined by the DMol3 Software

Table 5. Energies of PTT and TTD Molecules Calculated by MD and MC Simulations

Energies	PTT (eV)	TTD (eV)
Total energy	-81,561.308	-93,653.461
Binding energy	54,229.032	82,665.634
Interaction (adsorption) energy	-54,229.032	-82,665.634
Deformation energy	-25,233.488	-38,873.238
Rigid adsorption energy	-28,995.856	-43,792.396
Inhibitor energy	-27,332.326	-10,987.826
Kinetic energy	-3,885.360	-4,608.067
Electrostatic energy	810.1432	409.5462
Determined energy	929.2341	984.7684

**Figure 8. MC Simulations of PTT and TTD Molecules Bound to the Cu/Zn (111) Surface; Side View, Top View, and Dimensions**

MD and MC simulations were employed to identify the preferred adsorption sites on the Cu/Zn surface, under-

stand the surface inhibition processes, and identify the adsorption energy [25]. Figure 8 represents the top and

lateral views of the adsorption of PTT and TTD onto the Cu/Zn (111) surface. The inhibitor molecules were notably closer to surface and oriented themselves in a nearly flat plane and completely parallel to the Cu/Zn (111) surface after tuning at 200 ps and 300 K. The flattened form of the compounds confirms that the surface is covered and protected from the corrosion medium due to the electron donation from active centers of the PTT and TTD as well as N, O, and S to Cu and Zn orbitals. The adsorption energy (E_{ads}) of the inhibitor molecule is the sum of two types of energy, namely, deformation energy (E_{def}) and rigid adsorption energy (E_{Rigid}). Negative values of these energies indicate increased binding affinity between PTT, TTD, and the Cu/Zn surface. When the E_{ads} is more negative, the binding energy is more positive, making the molecule more easily adsorb on the surface. Elevated binding energies were obtained for PTT and TTD; binding energy was higher for TTD compared to PTT, confirming that it adsorbs most easily on the Cu/Zn (111) surface and

provides enhanced protection during inhibition, so the inhibitor energy was high. Notably, the more negative the interaction energy, the greater the binding affinity between PTT or TTD inhibitors and the Cu/Zn surface [23, 29]. PTT and TTD molecules demonstrate enhanced efficacy in preventing Cu/Zn corrosion by forming strong chemical bonds with the Cu/Zn (111) surface [25]. The E_{ads} values were large, implying spontaneous binding between each PTT or TTD and the surface. The binding energies of PTT and TTD on the surface were much greater than the determined energy, suggesting the stability of the molecules [35, 36]; all results are shown in Table 5. PTT and TTD formed close and packed monolayers in a regular manner that penetrated the entire surface area (Figure 8). The difference between the MD and MC findings was that MD showed TTD as unstable due to the breaking of bonds, as was shown in the final simulation system structure of MD (Figure 9); simultaneously, the PTT was shown as stable (Figure 10).

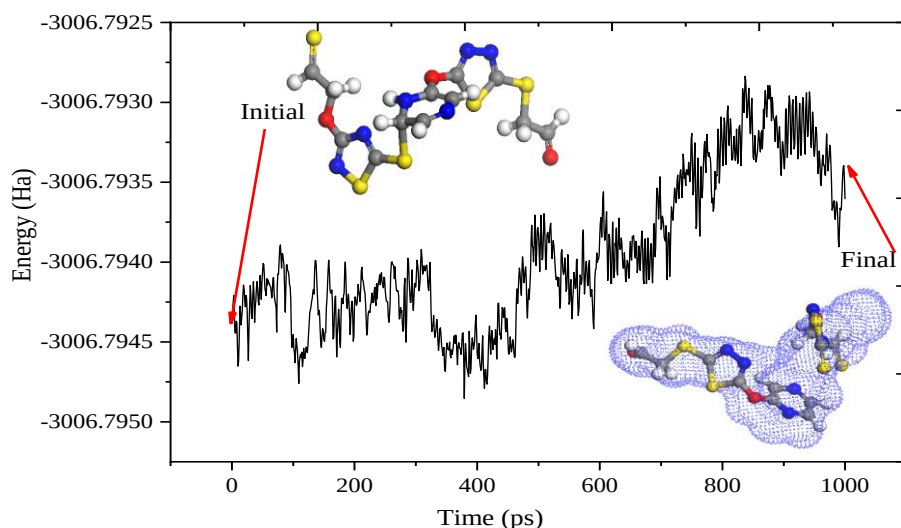


Figure 9. The Initial and Final Simulation System Structures of the TTD Compound in Molecular Dynamics

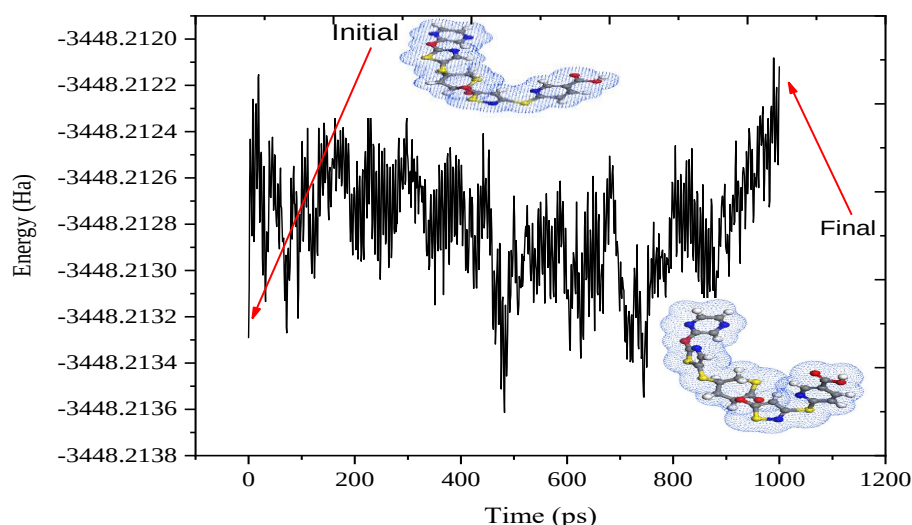


Figure 10. The Initial and Final Simulation System Structures of the PTT Compound Derived Via Molecular Dynamics

Additionally, the MD simulation provides data on adsorption, deformation, binding, and rigid adsorption energies, explaining that the increased binding affinity between PTT or TTD with the Cu/Zn surface was due to the molecules adsorbing more easily. The MC simulation illustrates how molecules adsorb onto the surface; due to electron donation to the Cu orbitals, the molecules align themselves in a nearly flat plane and are perfectly parallel to the surface.

Conclusion

In conclusion, our main approach in this study was theoretical; the adsorption, inhibition, ionization, and binding energies obtained show that both molecules PTT and TTD were active against corrosion; in particular, TTD was more effective than TTP. The inhibition depended on the mechanism of adsorption at the metallic surface and the nature of the heteroatoms within the structures. MC simulations were employed to evaluate corrosion inhibition efficiency. PTT and TTD could form proximal and packed monolayers and regularly penetrated the entire copper-zinc surface. The surface electrostatic potential referred to the molecules that possessed heteroatoms, which inhibited corrosion. The low values for each gap in energy and hardness indicated a stronger reaction and facilitated adsorption on the Cu/Zn (111) surface. The data presented demonstrated that TTP and TTD molecules effectively prevented Copper-Zinc alloy corrosion by blocking the associated pathways. TTD was unstable due to bond breaking, as shown in the final MD simulation system structure, whereas PTT remained stable.

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