Computational Study on Aluminum Corrosion Inhibitive Potentials of PreferredThiosemicarbazideDerivatives

Abstract

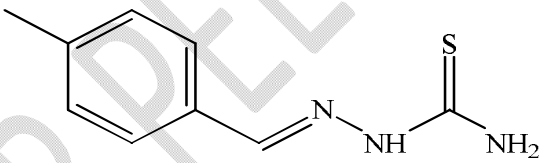
Aluminum has been a primary metal relic of cultural history since ancient times. They are still widely used today in many different industrial domains. Aluminum, however, is susceptible to the corrosion process in harsh conditions. Numerous traditional protective inhibitors have been developed to counteract this harmful behavior. Sadly, these preventive inhibitors come with several major side effects, including high costs and negative impacts on the environment and human health. Density functional theory (DFT) evaluations were used to examine the potentiality of the E extensively)-2-(4-methylbenzylidene)hydrazinecarbothioamide (MBHC) and N-phenylhydeazinecarbothioamide (PHC): toward the corrosion inhibition of the aluminum surface. The sulfur and nitrogen atoms over the structures of the compounds under investigation were nucleophilic, as indicated by the electrostatic potential (ESP) analysis results. The superior corrosion inhibitor preference of MBHC over PHC was demonstrated by the frontier molecular orbital theory results. Following the identification of the optimal MBHC − Al (111) and PHC − Al (111) complex configurations, Monte Carlo simulations were carried out. Remarkably, the MBHC demonstrated a wider range of competence in the corrosion inhibition process of Al (111) than the PHC, as demonstrated by the adsorption energy values of − 461.73 and −163.43 eV, respectively. These results offer a basis for the creation of environmentally friendly inhibitors that prevent corrosion on aluminum surfaces.

Keywords: adsorption energy; DFT; Potentials; Aluminum; inhibitor; Simulation

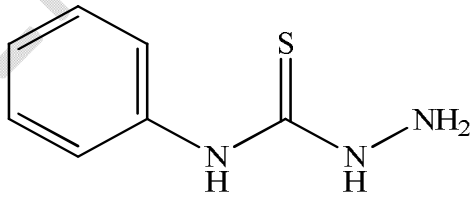
Introduction

In the crust of the globe, aluminum is the third most frequent metal overall and the fourth most prevalent in the crust specifically. After iron, aluminum is typically regarded as the second most significant metal. It has unique mechanical characteristics because of its low density (2.7 gcm^{-3}), which is just about one-third that of mild steel. As a result, aluminum and its alloys offer a high strength-to-weight ratio. In addition, a wide range of metal machining processes can be readily applied to them, and they exhibit good electrical and thermal conductivity. Furthermore, aluminum and its alloys have been fully recycled and reused, meaning that the items made from recycled metal are similar to those that were made before recycling in terms of quality and attributes [1]. Because of its excellent strength-to-weight ratio and affordable price, aluminum and its alloys are widely used in aerospace, automotive, electrical parts, building, packaging, and chemical industries[2-4]. In non-aggressive conditions, an Al_2O_3 coating naturally forms on the alloy surface to preserve aluminum.[5] Because of its numerous flaws and pores, the oxide layer is rapidly dissolved by corrosive OH^- or Cl^- ions. However, because key alloy components like copper and magnesium are present, aluminum and its alloys are highly susceptible to localized corrosion in harsh conditions. This alloy's microstructure is rather complicated, and several phases with different compositions have been found [6]. Since an oxide layer forms on aluminum and prevents the metal from oxidizing further, aluminum has a high level of corrosion resistance in both aqueous solutions and the environment. However, in some conditions, such as acidic

media, aluminum becomes extremely prone to corrosion. There are already several efficient protection techniques available, including surface coatings, organic inhibitor addition, anodic oxidation protection, and plasma electrolytic oxidation protection [7-9]. Inhibitors, which prevent corrosion on metal surfaces by forming a protective coating on them, are the most widely used and least expensive of them across a variety of industries. Products with an organic base are frequently used to prevent corrosion. Organic compounds with heteroatoms (N, S, and O) in a conjugated system exhibit excellent efficacy in preventing metal corrosion [10-12].The effectiveness of corrosion inhibition has been precisely established by experimental research, however, the precise mechanism by which inhibitors contribute most to corrosion inhibition has not been thoroughly addressed. Costs and time for research are significant. These issues are bridged by the theoretical study, which is now backed by sufficient hardware and software. The electron density of the molecule determines the corrosion inhibition efficiency, and theoretical research can determine this density with high accuracy. When evaluating corrosion inhibition in a molecule, theoretical research is just as important as actual research. Questions concerning experimental results based on the interactions of organic inhibitors with metal surfaces can be addressed using quantum chemical computations. [13,14] The performance of each inhibitor concerning its structure and orientation, as well as the mechanism by which an inhibitor clings to metal surfaces, may be fully explained by the use of the methods of density functional theory and Monte Carlo simulation [15, 16]. The corrosion inhibition of E)-2-(4-methylbenzylidene)hydrazinecarbothioamide (MBHC) and N-phenylhydeazinecarbothioamide (PHC): on Al (111) surfaces are studied in this work, along with the impacts of quantum parameters and the molecule's adsorption process.



(*E*)-2-(4-methylbenzylidene)hydrazinecarbothioamide (MBHC)



N-phenylhydrazinecarbothioamide (PHC)

Fig 1 : Structure of E)-2-(4-methylbenzylidene)hydrazinecarbothioamide (MBHC) and N-phenylhydeazinecarbothioamide (PHC)

2.1 Computational Investigations

2.1.1 DFT Study

Studies on corrosion inhibition commonly employ the density functional theory (DFT). When it comes to organic compounds' ability to suppress corrosion, the DFT approach provides an accurate description.Predicting the chemical properties of chemical species, such as the maximum occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO), electron affinity (A), ionization potential (I), energy gap (ΔE), hardness (η), fraction of electrons transferred (ΔN), softness (σ), and electronegativity (χ), is the main goal of research on inhibitors. The following paper used theoretical calculations to anticipate the effectiveness of the Thiosemicarbazide derivatives E)-2-(4-methylbenzylidene)hydrazinecarbothioamide (MBHC) and N-phenylhydeazinecarbothioamide (PHC): Employing the Gaussian 09W programming suite, the B3LYP technique coupled to 6-311G+(d,p) basis sets were utilized to optimize all compounds geometrically. This approach is widely used in the research of organic corrosion inhibitors. Then, several relevant global and local variables of the molecule's electronic configuration were computed. The I, A, ΔE, ΔN, η, σ, χ, $E_{LUMO,}$ and E_{HOMO} as well as maps of electrostatic potential were also computed [14,17].

$$A = E_{LUMO} \quad (1)$$

$$I = E_{HOMO} \quad (2)$$

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (3)$$

$$\eta = \left(\frac{\delta^2 E}{\delta N^2}\right)_v = \left(\frac{\delta \mu}{\delta N}\right)_v = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (4)$$

$$\sigma = 2\left(\frac{\delta N}{\delta \mu}\right)_{v(r)} = \frac{1}{\eta} = \frac{2}{\Delta E E_{LUMO} - E_{HOMO}} \quad (5)$$

$$\chi = \frac{-(E_{HOMO} + E_{LUMO})}{2} \quad (6)$$

$$\Delta N = \frac{(\chi_{Al} - \chi_{inh})}{2 \times (\eta_{Al} - \eta_{inh})} \quad (7)$$

Where, χ_{Al} = 4.26 eV and χ_{inh}= absolute electronegativities of the aluminum and inhibitor respectively.η_{Al} = 0 eVand η_{inh} = absolute hardness of the aluminum and inhibitor respectively.

2.1.2 Monte Carlo simulation.

The interactions between the chemical compounds and metal surface were theoretically studied by the Monte Carlo simulationThe simulation was conducted in Material Studio 2020 (Biovia, USA) using COMPASS force-field (condensed phase), on the Al (111) surface (three dimensions to the slab model) under periodic boundary conditions. The energies and chemical adsorption mechanisms components were calculated using the Ewald and atom-based summations, or responsibly to the Adsorption Locator module, built-in Materials Studio 2020 which used Monte Carlo simulations to pinpoint the most stable arrangement of the adsorbates on the Al (111) surface is the most stable of the many aluminum surfaces [18, 19],

3.1 Results

3.1.1 DFT Results

Table 1 is a list of the calculated quantum chemical parameters. Given structures that are optimized HOMO and LUMO density distribution of PHC and MBHC, Figure 2 shows that PHC has fewer adsorption centers than MBHC, indicating that MBHC has a higher capacity for high-protective adsorption. As a result, the high E_{HOMO} energy increases the inhibition performance by reflecting a greater connection between the molecule and the metal surface through the donor-acceptor process. [16, 20] MBHC can readily interchange electrons with the iron surface, as evidenced by its higher E_{HOMO} value of −0.218 eV compared to PHC's −0.210 eV. On the other hand, the fact that MBHC has a lower E_{LUMO} value indicates that it is an excellent inhibitor of electron acceptance and supports its superior performance (−0.018 eV) over PHC (−0.042 eV) [17, 21]. Better adsorption on aluminum surfaces is indicated by the narrower energy gap (ΔE) of MBHC (0.1493 eV) [22]. Further quantum chemical characteristics were derived, including ionization potential ($I = -E_{HOMO}$), electron affinity ($A = -E_{LUMO}$), global softness (σ), global hardness (η), electronegativity (χ), and number of electron transfer (ΔN). The literature claims that a molecule with a high (η) value is less reactive, whereas a high (χ) value indicates that the molecule may find it difficult to transfer its electrons to an acceptor [23, 24].The findings in Table 1 demonstrate that MBHC has lower (η) and (χ) values than PHC, indicating that it is more reactive and can transfer electrons through donor-acceptor interactions with metal molecules. [25]. Within a group of inhibitors, the electron donation tendency is described by the charge transfer rate ΔN. According to Lukovits [24, 26], the efficiency of the inhibition increases as the electron donor capacity at the steel/electrolyte increases if $\Delta N < 3.6$. Table 1 displayed ΔN values are all 3.6 lower than the original values. Therefore, the quantum chemical characteristics of MBHC performed better at its level of inhibition than the PHC inhibitor.

Table 1. The quantum chemical variables for MBHC and PHC inhibitors using the B3LYP/6-31G+ (d, p) basis set.

C	E_{LUMO}	E_{HOMO}	ΔE	H	Σ	χ	ΔN_{Al}
MBHC	-0.0180	-0.2178	0.1493	0.0747	13.40	0.143	-20.66
PHC	-0.0422	-0.2095	0.1673	0.0837	11.95	0.0948	-18.54

Inhibitor MBHC PHC

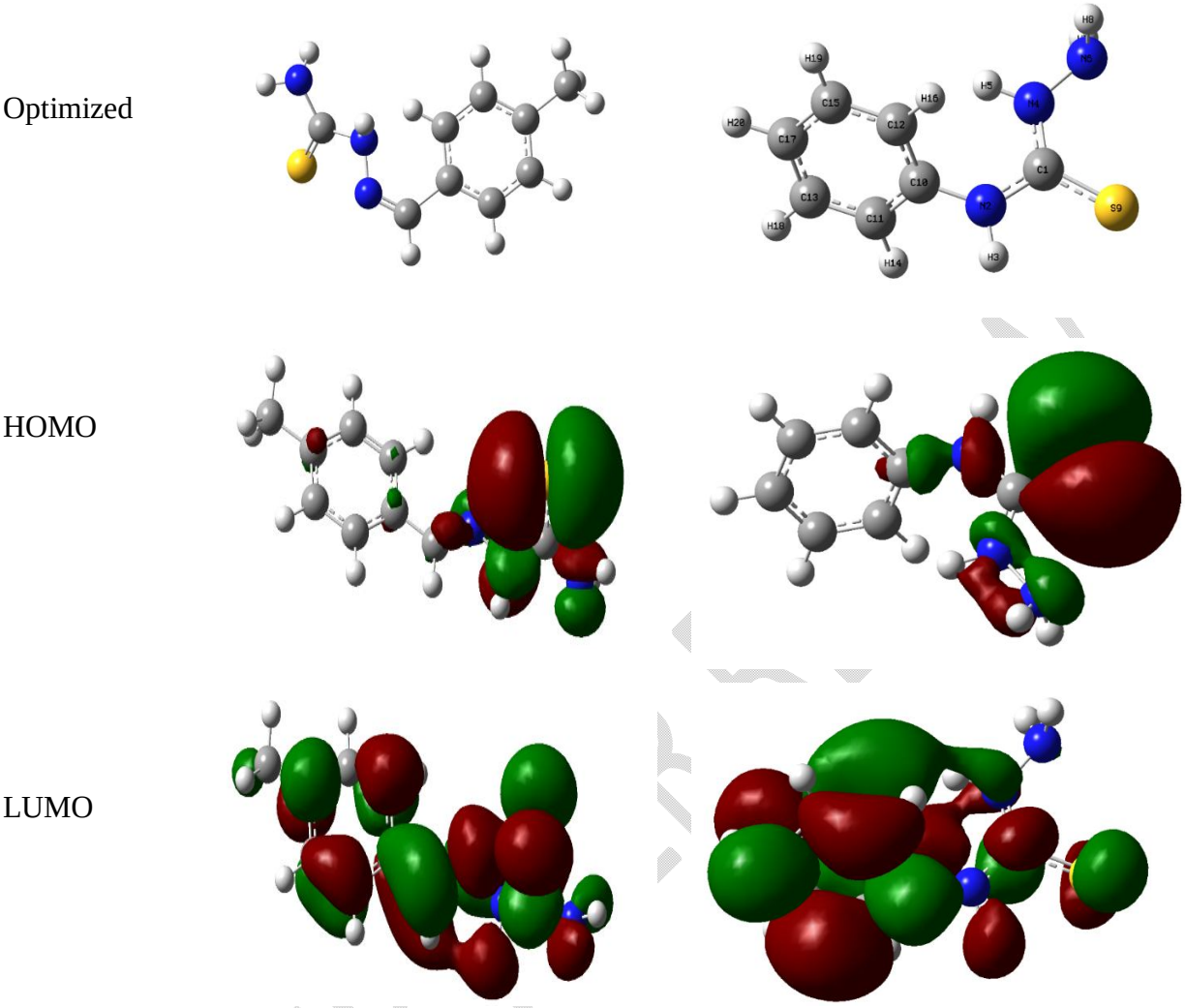


Figure 2The frontier molecular orbital density distribution for MBHC and PHC investigated compounds (Optimized, HOMO, and LUMO)

3.1.2 Electrostatic Potential (ESP) Map

ESP mapdisplays the three-dimensional charge distribution of the molecule (Figure 3). This map aids in the visualization of the molecule's variable charge areas, which helps forecast electrophilic and nucleophilic molecule-attack scenarios [27]. The highest positive region vulnerable to nucleophile assault is shown as blue in the ESP plot. On the other hand, the negative region that is vulnerable to electrophilic attack is shown in red. The MBHC and PHCsulfur and nitrogen atomsare found to have the highest electron density. Consequently, it is expected that these atoms will actively participate in the adsorption process on the Aluminium surface.

Inhibitor ESP maps Surface contour

MBHC

PHC

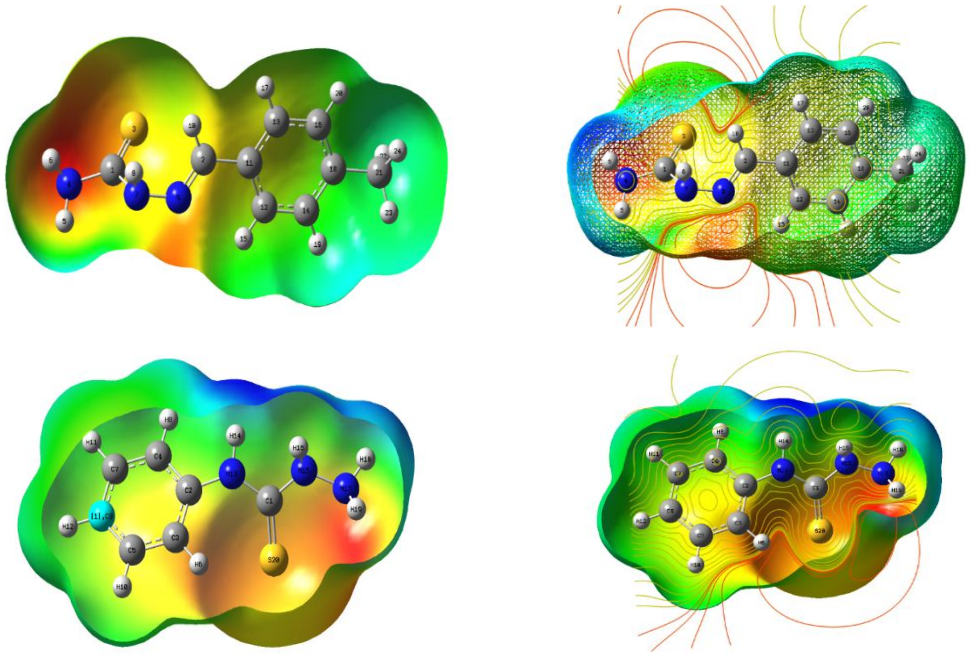


Figure 3.ESP maps and surface contours illustration of the MBHC and PHC investigated

3.1.3 Monte Carlo simulation.

To reduce the amount of contact area between the metal surface and corrosion-causing materials (such as water, acidic, or alkaline media), molecules need to align their structures as closely as possible in parallel to the metal surface. Adsorption is the term for this process. Therefore, Monte Carlo simulation was applied to determine and identify the inhibitors under evaluation and their ability to adsorb onto the surface of Al (111). Figure 4 shows the optimal MBHC and PHC adsorption mode on the aluminum surface under study.

Table 2 displays the molecule under investigation's adsorption characteristics, which include total energy, rigid adsorption energy, adsorption energy, and deformation energy. We have previously defined these parameters [18, 24] in our previous work. The total rigid adsorption energy before and after an adsorbate's surface relaxation is known as the "adsorption energy," and it is the most significant energy characteristic in adsorption. Table 2 indicates that the inhibitor attaches to the surface of Al(111) spontaneously based on the negative value of the adsorption energies [19]. The differential adsorption energy (dE_{ad}/dN_i), which is the energy needed or released to remove a portion of the adsorbate (i.e., desorption energy), is defined by assuming that the surface energy of Al is zero. The inhibitor's adsorption energy of -461.73 kcal mol^{-1} for MBHC and 163.43kcal mol^{-1} for PHC and its desorption energy of --461.73 kcal mol^{-1} (MBHC) and –80.754 kcal mol^{-1} (PHC) indicate that the adsorption process is substantially preferred. The inhibitor preferentially adsorbs on the Al(111) surface with little to no competition because it adsorbs with significantly less energy, even in the presence of water (--4.28 $kcalmol^{-1}$) [24, 28].

Table 2 Results and descriptors measured by the Monte Carlo simulation for adsorption of MBHC and PHC molecules on Al (111)

Compound	dEad/dNi	Adsorption energy	Rigid adsorption energy	Deformation energy	Total energy
MBHC	-461.73	-461.73	-30.707	-431.02	-3.272
PHC	-80.75	-163.43	-55.83	-107.61	-5.75
Water	-4.281	-8.297	-7.346	-0.950	-7.346

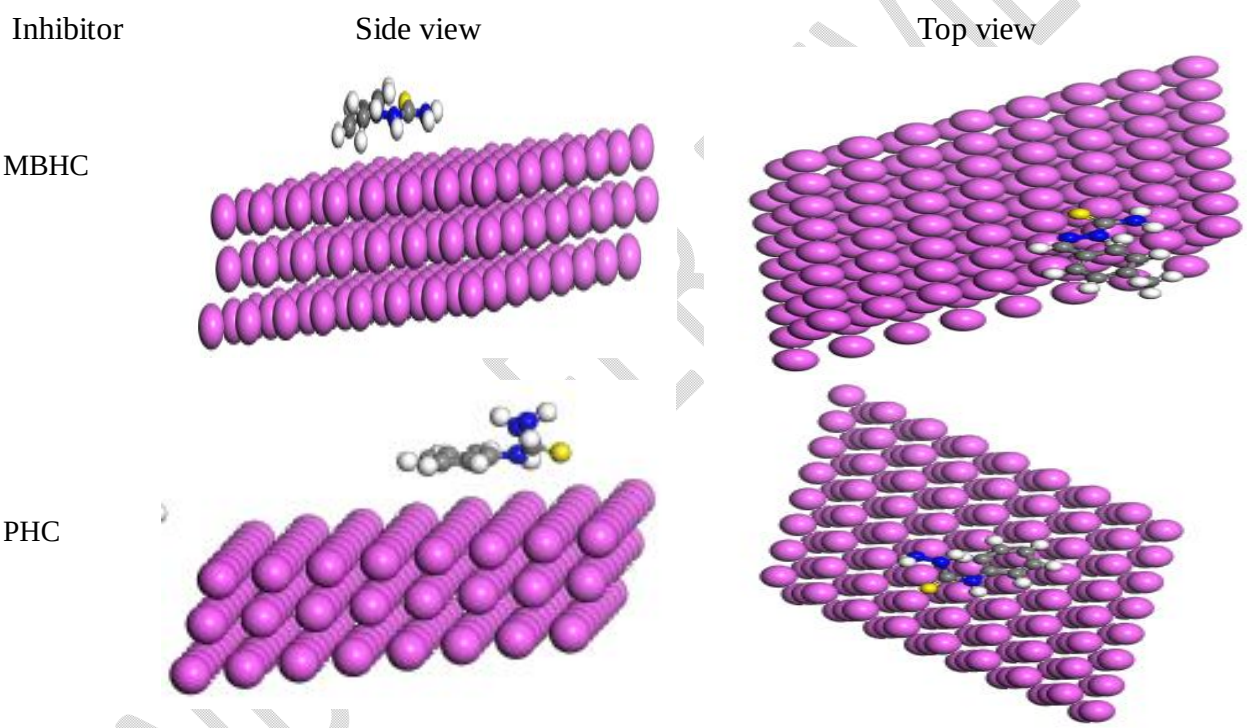


Figure 4The most appropriate conformation for adsorption of the MBHC and PHC molecules on Al (111)

4. Conclusion

The corrosion inhibition potential of E)-2-(4-methylbenzylidene)hydrazinecarbothioamide (MBHC) and N-phenylhydeazinecarbothioamide (PHC) was analyzed and measured using density functional theory calculations employing the B3LYP/6-31G+ (d,p) basis set. This was done to determine whether these compounds had a potentially strong ability to inhibit corrosion in aluminum and its alloys. In contrast to PHC, MBHC has a lower electronegativity and ΔE, (0.1612 eV)values, which may be attributed to the presence of an aromatic ring and heteroatom in its structure, which demonstrated a stronger and mutual connection between the inhibitor and

the metallic surface according to the results of the Density Functional Theory analysis:Furthermore, the results showed that MBHC had the largest ΔN value (0.258232 eV), indicating improved chemical stability and reactivity. In light of this, MBHC is more likely than PHC to react as an electron donor.de, which effectively inhibits the corrosion of alloys including aluminum. MBHC was predicted by Monte Carlo simulations to function as a more potent anti-corrosion agent than PHC, particularly in acidic environments.

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