

## Computational study of some heterocyclic compounds as anti-corrosion agents for aluminum using DFT method

### Abstract

DFT Calculations were performed on Oxazole, Pyrazole, Imidazole, Isoxazole, Thiazole and Isothiazole as corrosion inhibitors for Al with full optimization of geometries in DFT-B3LYP/6-31 G\*Level (d, P) to find a relation between the molecular structure and corrosion inhibition. The electronic properties such as the energy of the highest molecular orbital that is occupied (HOMO), the energy of lowest unoccupied orbital (LUMO), the energy gap (LUMO–HOMO), quantum chemical parameters such as hardness, softness, the fraction of the electron transferred, and the electrophilicity index. In order to know the relationship of molecular structure and corrosion inhibition on surface of the quantum chemical parameters, boundary orbital's isothiazole has been found the highest anti-corrosion efficiency as compared to other

Keywords :Al , DFT, Corrosion, heterocyclic compounds, inhibitor

### Introduction

Automobiles, aviation, domestic appliances, packaging, and electrical devices all employ aluminum as a material [1,2]. The quick development of oxide coatings on the surface of aluminum accounts for its resistance to corrosion in aqueous conditions. In the presence of corrosive acids, however, aluminum is easily corroded [1,2]. Because of its wide range of applications, research into the corrosion behavior of aluminum in many harsh settings has remained popular. Hydrochloric acid is one of the most often used industrial chemicals, and it corrodes metals like aluminum. As a result, inhibitors are required to slow down the metal dissolving process [3] among several techniques used in mitigating corrosion problems, the use of chemical inhibitors remains the most cost-effective and practical method [4]. In the realm of corrosion chemistry, the development of aluminum corrosion inhibitors based on organic molecules is gaining popularity.[ 5]. The reason for this is that, despite the fact that inorganic substances such as phosphates, chromates, and dichromates are inorganic, inorganic substances such as phosphates, chromates, and dichromates are organic

and arsenates have been proven to be effective as metal corrosion inhibitors, but their main disadvantage is their toxicity, which has led to harsh condemnation of their use [6]. Organic inhibitors have been demonstrated to be practical and helpful since they are effective, environmentally friendly, and relatively inexpensive [7–8] and are more effective than inorganic chemicals [9].

## Methodology:

Theoretical calculations of the quantum chemical parameters were carried out employing comprehensive geometry optimizations the standard Gaussian-09 software package<sup>39</sup>. Optimizations to the geometry were made using B3LYP functional at the 6-31G\* (d,p) basis set and at the density functional theory (DFT) level.

## Results and Discussion

The inhibitor's efficacy could some heterocyclic compounds be determined from the quantum chemical parameters calculated from the optimized structure. These global parameters include the frontier Molecular Orbital's :  $E_{HOMO}$  (the molecular orbital with the most occupied molecular orbital) and  $E_{LUMO}$  (the lowest molecular orbital that isn't occupied ; the energy gap ( $\Delta E_{gap}$ ) between  $E_{HOMO}$  and  $E_{LUMO}$ ; the global hardness ( $\eta$ ) of the inhibitor; the softness ( $\sigma$ ); the fraction of the electron transferred ( $\Delta N$ ); the electrophilicity index ( $\omega$ ) is a measure of how electrophilic a substance is.

These global parameters include the frontier Molecular Orbital's on Al According to Koopman's theorem[10] , the absolute electronegativity ( $\chi$ ), the absolute hardness ( $\eta$ ), the softness ( $\sigma$ ) and the electrophilicity index ( $\omega$ ) are given as follow[11]:

$$\omega = \frac{\mu^2}{2\eta} \quad , \quad (\mu = -\chi)$$

$$\chi = \frac{I+A}{2} \quad , \quad \chi = -\frac{E_{HOMO}+E_{LUMO}}{2}$$

$$\eta = \frac{I-A}{2} \quad , \quad \eta = -\frac{E_{HOMO}-E_{LUMO}}{2}$$

$$\sigma = 1/\eta$$

where the electron affinity (E) and the ionization potential (I) are calculated using the following relations according to the Molecular Orbital theory.

$$I = -E_{HOMO} \quad , \quad A = -E_{LUMO}$$

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

The absolute electronegativity ( $\mu$ ) is considered to be equal to the negative of the chemical potential ( $\chi$ ). Parr proposed the concept of an inhibitor's electrophilic power ( $\omega$ ). [12] Herein, electrons flow from the less electronegative inhibitor ( $\chi_{inh}$ ) to higher electronegative Aluminum ( $\chi_{Al}$ ) until the chemical potentials become equal. The number of electrons transported from the inhibitor to the metallic surface ( $\Delta N$ ) was estimated using the values of  $\chi$  and  $\eta$  as well. follow[13]:

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

where  $\chi_{Al}$  and  $\chi_{inh}$  signify the absolute electronegativity of Al and the inhibitor, respectively, and Al and inh denote the absolute hardness of Al and the inhibitor. The electron transport is driven by the difference in electronegativity ( $\chi_{Al} - \chi_{inh}$ ), whereas  $(\eta_{Al} + \eta_{inh})$  acts as resistance [14]. In this study, the theoretical values of  $\chi_{Al} = 3.2093 \text{ eV}$  and  $\eta_{Al} = 2.7764 \text{ eV}$  were used to calculate the number of electrons transferred [15]. All calculations have been performed for the molecules in the gas phase.

The inhibitors' frontier Molecular Orbitals (FMO) demonstrate the molecule's potential to adsorb on metal surfaces [16].  $E_{HOMO}$  refers to a molecule's ability to donate electrons to an acceptable acceptor level of inhibitor with vacant metal d-orbitals. Its ability to receive electrons is indicated by the letter  $E_{LUMO}$ . As a result, a lower  $E_{LUMO}$  value indicates that the molecule has a greater potential to receive electrons, resulting in improved inhibitor efficiency [17]. As a result, boosting the HOMO energy while decreasing the LUMO energy increases the inhibitor's capacity to bind to the metal surface.

Table 1. The DFT approach was used to calculate the inhibitors' (HOMO-LUMO) energies

Compounds	HOMO	LUMO
Al	-5.9857*	-0.4328*
Imidazole	-6.3598	0.6522
Pyrazole	-6.7286	0.3806
Oxazole	-7.2616	-0.4745
Isoxazole	-7.5438	-0.9140
Thiazole	-7.1346	-1.0492
Isothiazole	-7.2614	-1.2841

[18]\*

Chemical reactivity is a consequence of the interaction between the HOMO and LUMO levels of the reacting species, according to the frontier molecular orbital (FMO) theory [19,20].  $E_{HOMO}$  is a quantum chemical parameter that refers to a molecule's ability to donate electrons. A high  $E_{LUMO}$  value is likely to suggest that the molecule has a low empty molecular orbital energy tendency [21].  $E_{LUMO}$ , or the energy of the lowest unoccupied molecular orbital, reflects the molecule's ability to

receive electrons [22]. As a result, the lower the value of  $E_{LUMO}$ , the more electrons the molecule accepts. As a result, as the HOMO and LUMO energy values grow, the inhibitor's ability to attach to the metal surface increases.

Table 2: The calculated HOMO-LUMO gap interaction of Al with the inhibitors.

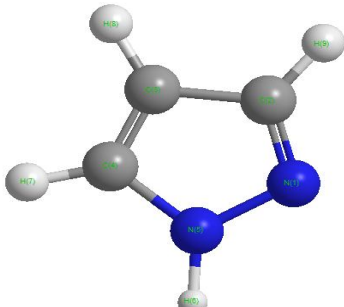
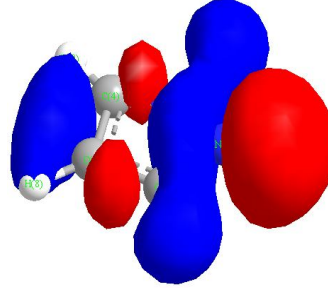
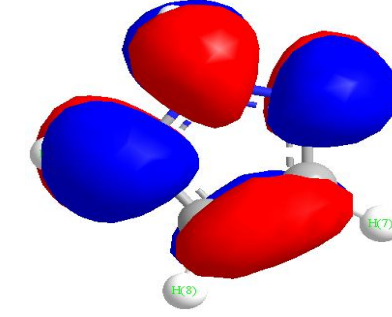
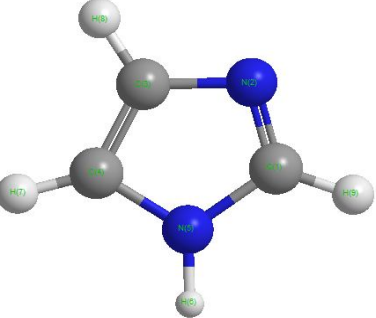
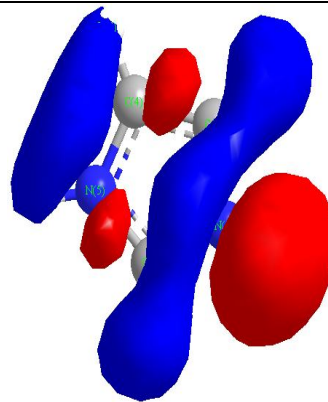
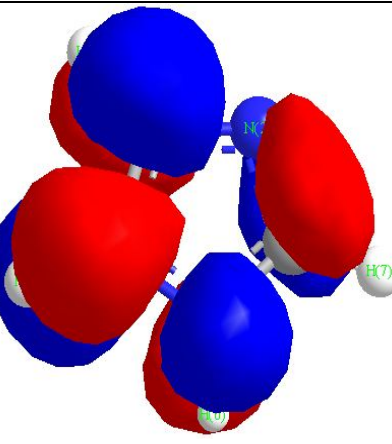
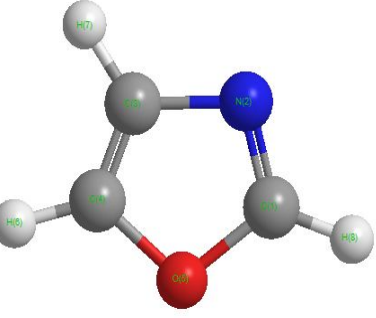
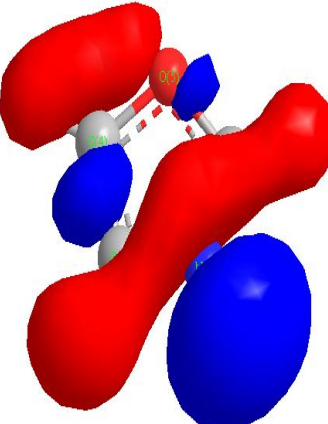
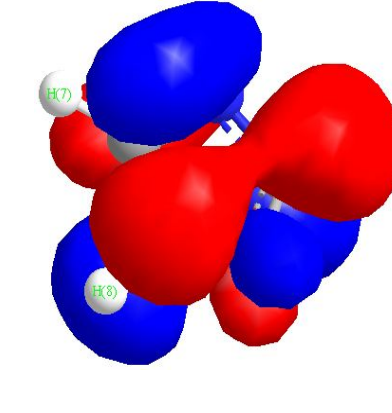
Inhibitors	$(LUMO)_{Inh} - (HOMO)_{Al}$ (eV)	$(LUMO)_{Al} - (HOMO)_{Inh}$ (eV)
Imidazole	6.6379	05.927
Pyrazole	6.3663	6.2958
Oxazole	5.5112	6.8288
Isoxazole	5.0717	07.111
Thiazole	4.9365	6.7018
Isothiazole	4.7016	6.8286

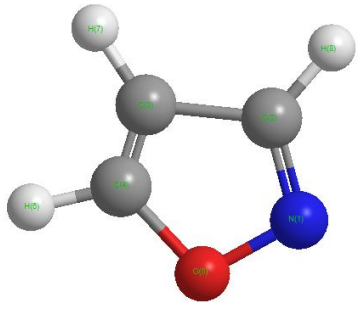
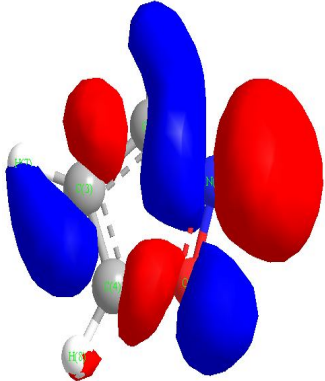
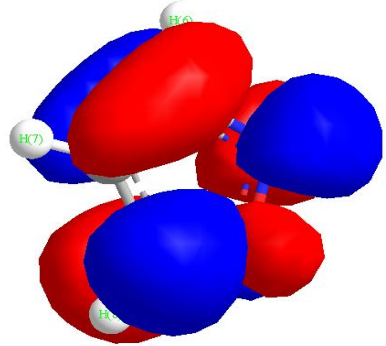
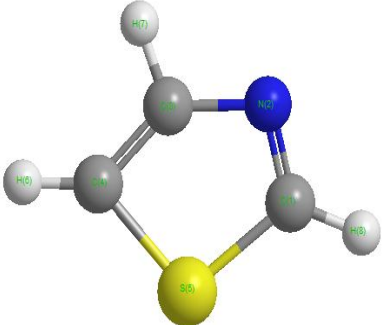
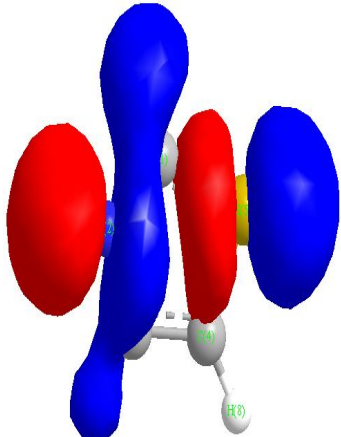
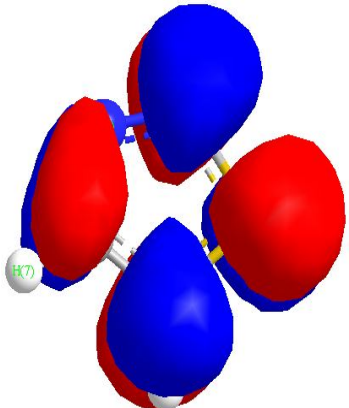
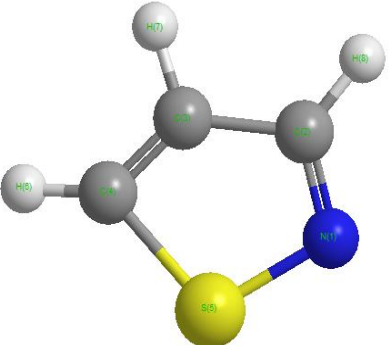
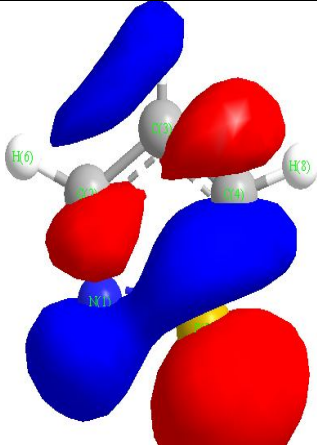
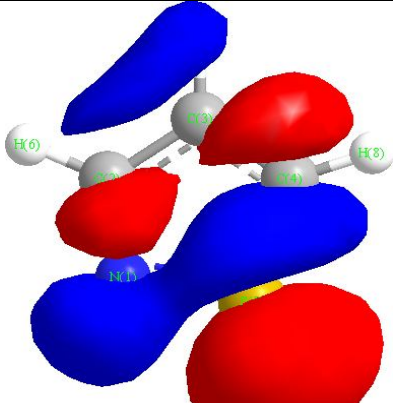
Aluminum acts as a Lewis base, whereas the inhibitors Isoxazole, Thiazole, and Isothiazole act as Lewis acids, as shown in Table 2. As a result, Aluminum will use the HOMO orbital of the Isoxazole, Thiazole, and Isothiazole to commence the reaction with the LUMO orbital of the Isoxazole, Thiazole, and Isothiazole. Because the  $LUMO_{inh} - HOMO_{Al}$  gap values are between 4 and 5 eV, the interaction will have an ionic character. Only if the  $LUMO_{inh} - HOMO_{Al}$  gap is close to zero can a strong covalent bond be expected [23,24]. Oxazole, Pyrazole, and Imidazole inhibitors operate as a Lewis base, while aluminum acts as a Lewis acid.

Thus Isoxazole, Thiazole, Isothiazole act as a cathodic inhibitor while Oxazole, Pyrazole, Imidazole act as an anodic inhibitor Table 3 show the calculated global reactivity parameters which were used to study the effectiveness of the inhibitors. The electronegativity ( $\chi$ ), global hardness ( $\eta$ ), global softness ( $\sigma$ ), proportion of electron transmitted ( $\Delta N$ ), and electrophilicity index ( $\omega$ ) of the molecules are among these metrics

The values of  $\Delta N$  represent the inhibition efficiency caused by the aluminum inhibitor's electron donating [25]. The capacity of these inhibitors to give electrons to the metal enhances their inhibition efficiency, and the bulk of the transferred electrons are connected with the best inhibitor, and ( $\omega$ ) indicates the inhibitor's ability to take aluminum electrons.

Figure1: HOMO & LUMO of the optimized fragments

inhibitor	Structure	HOMO	LUMO
Pyrazole	 <p>Ball-and-stick model of the Pyrazole molecule, showing a five-membered ring with two nitrogen atoms (blue) and three carbon atoms (grey), with hydrogen atoms (white) attached to the carbons.</p>	 <p>3D visualization of the Highest Occupied Molecular Orbital (HOMO) for Pyrazole, showing electron density lobes in blue and red.</p>	 <p>3D visualization of the Lowest Unoccupied Molecular Orbital (LUMO) for Pyrazole, showing electron density lobes in blue and red.</p>
Imidazole	 <p>Ball-and-stick model of the Imidazole molecule, showing a five-membered ring with two nitrogen atoms (blue) and three carbon atoms (grey), with hydrogen atoms (white) attached to the carbons.</p>	 <p>3D visualization of the Highest Occupied Molecular Orbital (HOMO) for Imidazole, showing electron density lobes in blue and red.</p>	 <p>3D visualization of the Lowest Unoccupied Molecular Orbital (LUMO) for Imidazole, showing electron density lobes in blue and red.</p>
Oxazole	 <p>Ball-and-stick model of the Oxazole molecule, showing a five-membered ring with one nitrogen atom (blue) and one oxygen atom (red), and three carbon atoms (grey), with hydrogen atoms (white) attached to the carbons.</p>	 <p>3D visualization of the Highest Occupied Molecular Orbital (HOMO) for Oxazole, showing electron density lobes in blue and red.</p>	 <p>3D visualization of the Lowest Unoccupied Molecular Orbital (LUMO) for Oxazole, showing electron density lobes in blue and red.</p>

<p><b>Isoxazole</b></p>	 <p>Ball-and-stick model of Isoxazole (C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>O). The structure shows a five-membered ring with two carbon atoms (grey), two nitrogen atoms (blue), and one oxygen atom (red). Hydrogen atoms are shown in white. Labels include C1, C2, N1, N2, O1, H1, H2, H3, H4, H5, H6, and H7.</p>	 <p>Orbital density plot of Isoxazole. The molecule is shown with red and blue lobes representing the positive and negative phases of the molecular orbitals. Labels include C1, C2, N1, N2, O1, H1, H2, H3, H4, H5, H6, and H7.</p>	 <p>Orbital density plot of Isoxazole, showing a different view of the molecular orbitals. Labels include H7, H6, H5, H4, H3, H2, H1, N1, N2, C1, C2, and O1.</p>
<p><b>Thiazole</b></p>	 <p>Ball-and-stick model of Thiazole (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>S). The structure shows a five-membered ring with two carbon atoms (grey), one nitrogen atom (blue), and one sulfur atom (yellow). Hydrogen atoms are shown in white. Labels include C1, C2, C3, N1, S1, H1, H2, H3, H4, H5, H6, and H7.</p>	 <p>Orbital density plot of Thiazole. The molecule is shown with red and blue lobes representing the positive and negative phases of the molecular orbitals. Labels include C1, C2, C3, N1, S1, H1, H2, H3, H4, H5, H6, and H7.</p>	 <p>Orbital density plot of Thiazole, showing a different view of the molecular orbitals. Labels include H7, H6, H5, H4, H3, H2, H1, N1, S1, C1, C2, and C3.</p>
<p><b>Isothiazole</b></p>	 <p>Ball-and-stick model of Isothiazole (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>S). The structure shows a five-membered ring with two carbon atoms (grey), one nitrogen atom (blue), and one sulfur atom (yellow). Hydrogen atoms are shown in white. Labels include C1, C2, C3, N1, S1, H1, H2, H3, H4, H5, H6, and H7.</p>	 <p>Orbital density plot of Isothiazole. The molecule is shown with red and blue lobes representing the positive and negative phases of the molecular orbitals. Labels include H7, H6, H5, H4, H3, H2, H1, N1, S1, C1, C2, and C3.</p>	 <p>Orbital density plot of Isothiazole, showing a different view of the molecular orbitals. Labels include H7, H6, H5, H4, H3, H2, H1, N1, S1, C1, C2, and C3.</p>

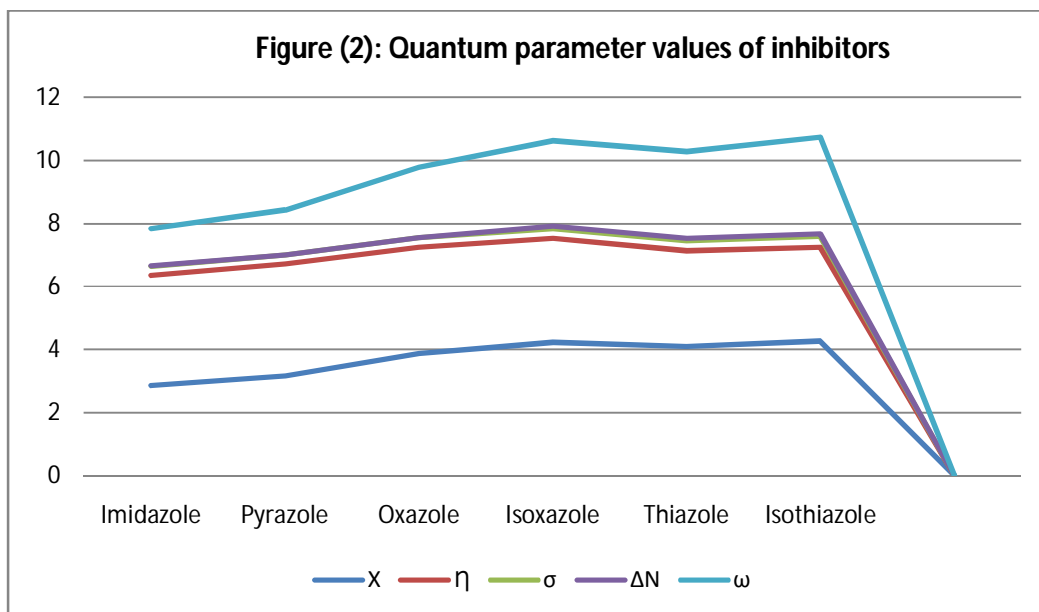
.Table 3: Quantum chemical properties of inhibitors were calculated

Quantum parameter	Imidazole	Pyrazole	Oxazole	Isoxazole	Thiazole	Isothiazole
$E_{HOMO}$	-6.3598	-6.7286	-7.2616	-7.5438	-7.1346	-7.2614
$E_{LUMO}$	0.6522	0.3806	-0.4745	-0.9140	-1.0492	-1.2841
$\Delta E(gap)$	007.01	7.1091	6.7871	6.6298	6.05854	5.9773
$I(eV)$	6.3598	6.7286	7.2616	7.5438	7.1346	7.2614
$A(eV)$	-0.6522	-0.3806	0.4745	0.9140	1.0492	1.2841
$X(eV)$	2.8538	03.174	3.8680	4.2289	4.0919	4.2727
$\eta(eV)$	03.506	3.5546	3.3935	3.3149	3.0427	2.9886
$\sigma$	0.2852	0.2813	0.2946	0.3016	0.3286	0.3346
$\Delta N$	0.0282	0.0027	0.0185	0.0837	0.0758	0.0922
$\omega$	1.1614	1.4117	2.2044	2.6974	2.7514	3.0542

$$X_{Al} = 3.2093, \eta_{Al} = 2.7764$$

Soft molecules have small  $\Delta E_{gap}$  whereas hard molecules have large  $\Delta E_{gap}$  based on (Hard-Soft-Acid-Base)hypothesis (HSAB) [26,27]. The most effective inhibitor for the metals is classified as a soft base[28]. As a result, the Isothiazole with the shortest  $E_{gap}$  and highest softness ( $\sigma$ ) is predicted to have the best. Calculating the inhibitor's softness ( $\sigma$ ) and thus its reactivity confirms this result. Table 3 shows that the isothiazole has the highest value compared to the others. In addition, it can be observed (Table 3) that the hardness ( $\eta$ ) of the Isot Thiazole has the smallest value of all fragments. This tendency is the reverse of what has been obtained for the softness ( $\sigma$ ). Consequently, the Isothiazole is the best inhibitor. The electrophilicity index ( $\omega$ ) indicates the ability of the inhibitor to accept electrons from Aluminum.

Compounds that can donate electrons to the metal surface's vacant orbitals to make coordinated covalent bonds, as well as absorb free electrons from the metal surface to establish bonds using their antibonding orbitals, are efficient corrosion inhibitors.



## CONCLUSIONS

Theoretical calculations gave a good picture of the compounds as aluminum corrosion inhibitors, and isothiazole showed greater inhibition efficiency compared to other inhibitors, as they were found to have higher values ( $\omega$ ) due to lower values of  $E_{LUMO}$ , which indicates their high acceptability. Electrons from aluminum.

The inhibition efficiency is increased due to the saturation and adsorption process on the aluminum surface, so the resulting inhibition efficiency order is

Isothiazole > Thiazole > Isoxazole > Oxazole > Pyrazole > Imidazole

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