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Predict the ability of inhibition corrosion by Azo-Schiff bases compounds derivatives

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Abstract

The current study investigates the compounds (2-7) physical characteristics, to choose the best corrosion inhibition. 6-311G/ (d, p) base set and Density Functional Theory (DFT) was utilized to estimate inhibitor efficacy. Physical characteristics such as ionization energy (dipole moment, softness, and hardness) are computed for compounds with occupied orbitals (energy gap), hardness (hardness), and softness (softness). Compound 7 is the most effective, followed by compound 5 with medium efficiency and (2) with the lowes efficiency. The (HOMO-LUMO) state and the total electron density (TED) are also discussed.

Keywords: DFT, Corrosion, Azo – Schiff bases, HOMO-LUMO

Introduction

Metal corrosion is a phenomenon that occurs when metallic surfaces interact with their surroundings, resulting in the breakdown of the metals. It is a pollution process that involves changing steel to a more chemically stable state or returning it to its ores, such as oxide or hydroxide (1). On the other hand, is the metal's progressive deterioration caused by chemical interaction with its surroundings. Corrosion is the disintegration of metal structures caused by their interaction with the environment (2). Metals are used to make various items, including pipes, constructions, and other things. Corrosion is a significant factor in the chemical industry since it is the root of many difficulties in production lines and is frequently the cause of malfunctions and production interruptions (3). Product leakage from corrosive units pollutes the environment and risks people's health. && Because of its mechanical qualities, mild steel is commonly used in the gas, oil, and chemical sectors, and steel is utilized in the industry because it is less expensive than anti-corrosive metals or alloys (4,5).

Despite this, contact with corrosion-causing circumstances, especially those containing chloride ions, causes this alloy to corrode. Inhibitors are compounds added to acidic, basic, or saline solutions in extremely minute amounts, measured in parts per million (ppm), via adsorption on metal surfaces, depending on the nature of the adsorbed metal surface and the media. The inhibitors function by slowing down the pace of mineral corrosion or oxidation (6-8). The most well-known technique of preserving metal surfaces from corrosion is to employ various inhibitors; Due to their exceptional anti-corrosion properties, chemical structure, and interactions with the metal surface, They are perhaps the most suitable materials in the industry. In recent years, heterocyclic derivatives, green organic molecules, and biological commodities have been used to reduce mild steel corrosion rates, according to a literature review (9-13). Even though consumers contain one or more atoms with high electron density in their structures, such as nitrogen, oxygen, sulfur, and phosphorous, and the presence of unsaturated bonds in the aromatic rings, five-member heterocyclic derivatives are commonly used as corrosion inhibitors to protect metallic corrosion in various solutions. Steel is the most important engineering material in the industry since it is used in many different applications, including equipment, buildings, automobiles, and other areas of our daily life. These constructions are made of different steel grades with different chemical compositions. (14-16). Due to its superior mechanical and physical properties, low- mild or carbon steel are among the most commonly used alloys in constructing various oil equipment. Corrosion is a problem for mild steel, as it is for other metals and alloys. (17). This study included suggested the inhibitions compounds of corrosion by quantum parameters.

Calculations models

This project made use of the Gaussian 09 software. A hybrid function of Becke three-parameters Lee, Yang, and Parr were used in the quantum chemical computations using Gaussian 09 tools and density functional theory (DFT) (B3LYP). Because it offers accurate electrical characteristics and geometries for many organic molecules, the 6-31G (d, p) basis range was utilized (as shown in Figure 1), with similar findings [18,19]. We used a vacuum medium for our computations [20].

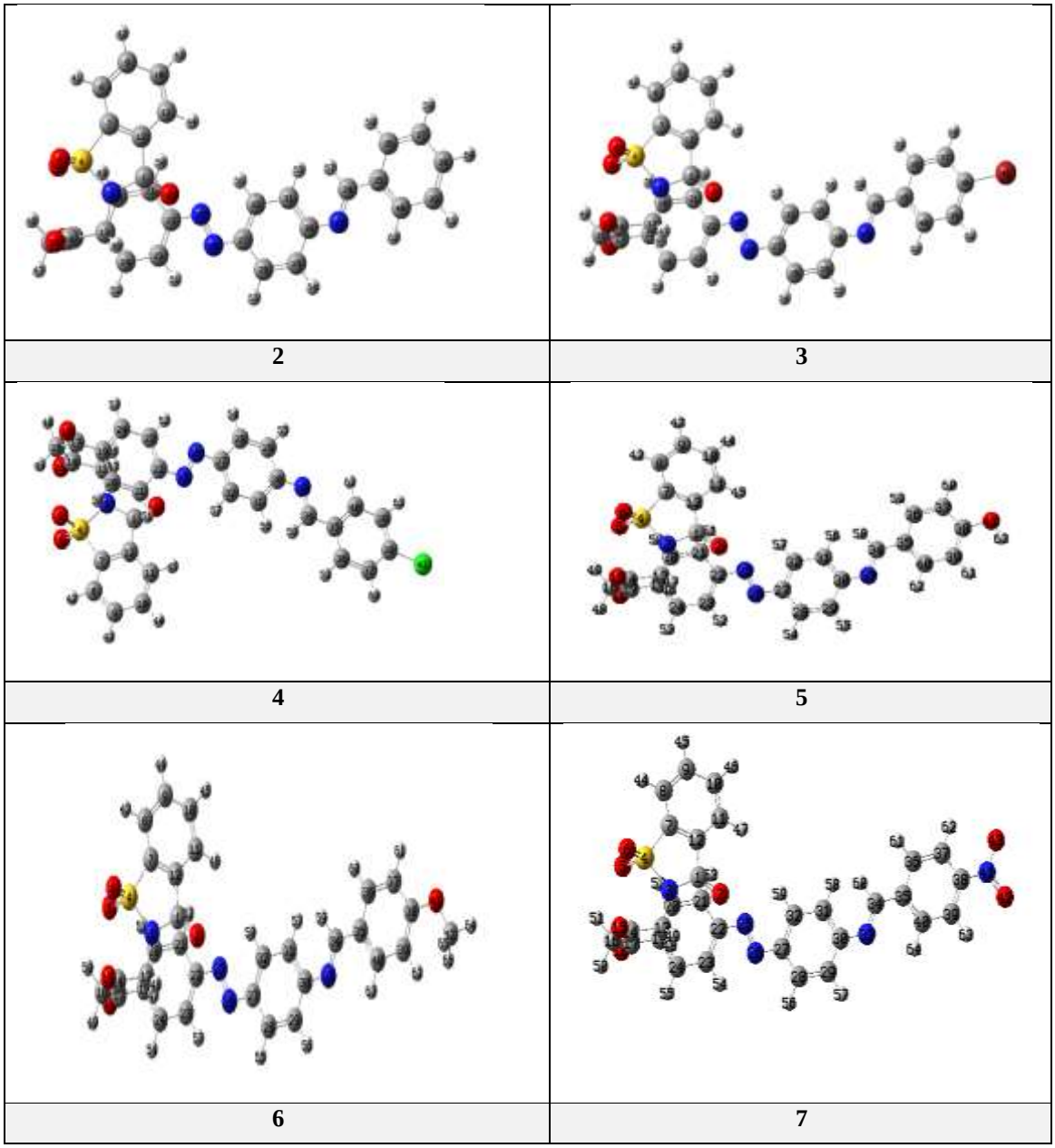


Figure 1: Equilibrium geometry of the inhibitor's molecules was calculated by DFT (B3LYP/6-311+G (d, p)) methods.

Theoretical results as corrosion inhibition

Inhibitors parameters

Molecular centers were found to be drawn to metal surfaces using the molecular Orbital Theory [21]. This theory predicted how absorbed inhibitor chemicals would interact with the metal surface. The inverse of the energy dependence of the stability of the difference in orbital energy, as ΔE = ELUMO-EHOMO, contributes to the authoritarian contribution via the Molecular orbital borders (FMO). Chemical inhibitors with high EHOMO values are more likely to donate electrons. An electron transfer capacity may be expressed as the energy HOMO (EHOMO). The LUMO energy (ELUMO) evaluates an electron-accepting potential by how well a molecule absorbs an electron. The energy gap (ΔE) between the orbital boundaries is another crucial component in characterizing molecular activity; as the energy gap narrows, the inhibitor's efficiency improves [22]. Tables 3 and 4 show the relationship between molecule inhibition efficiency and chemical quantum parameters such as the electrons' highest occupied molecular orbital (EHOMO), the lowest unoccupied molecular orbital energy (ELUMO), the energy gap (ΔE= ELUMO-EHOMO), electronegativity (χ), the dipole moment (μ), electron affinity (EA), the ionization potential (IP), and global softness (S).

electronic affinity (EA) and the ionization potential (IP) were linked to the negative HOMO energy and the LUMO energy, respectively, according to Koopman's hypothesis

$$IP = -E_{HOMO} \qquad 1$$

When removing an electron, the amount of energy available to remove it is known as the ionization potential (IP). Inhibition is very effective because of the low ionization energy.

$$EA = -E_{LUMO} \quad (2)$$

When an electron is delivered to a neutral atom, the quantity of energy released is referred to as EA. The less stable the system is, and the more effective inhibition is, the higher the value of electron affinity. The second derivative of the E, hardness (η), evaluates both the stability and reactivity of a molecule[23].

$$\eta = \frac{IP - EA}{2} \quad (3)$$

$$X = -\mu = \frac{IP + EA}{2} \quad (4)$$

The HOMO and LUMO energies were linked to these values. High inhibition efficiency is indicated by a low electronegativity value. Global softness (S) is the polar opposite of global hardness (H). The degree of softness is crucial in influencing the stability and reactivity of molecules.

$$S = \frac{1}{\eta} \quad (5)$$

Parr created the global electrophilicity index (ω), which is an estimate of the energy stability of a molecule after it absorbs an extra sum of electrons [24]. A score of 0 or below for the global electrophilicity index indicated a strong inhibitor.

$$\omega = \frac{(-X)^2}{2\eta} \quad (6)$$

The inhibition values according to quantum parameters ; HOMO was 5 > 6 > 2 > 4 > 3 >7, LUMO was 6 > 5 > 4 > 2 > 3 >7 ΔE was 7 > 3 > 4 > 2 > 5 > 6, μ was 6 > 5 > 2 > 4 > 3 > 3, IE was 5 > 6 > 2 > 4 > 3 > 7, EA was 7 > 3 > 4 > 2 > 5 > 6, χ was 6 > 5 > 2 > 4 > 3 > 6, η was 7 > 4 > 3 > 2 > 5 > 6, S was 7 > 3 > 4 > 5 > 2 > 6, and **ω** was 6 > 5 > 2 > 4 > 3 > 7. While the final order of the inhibitors efficiency was 7 > 6 > 5 > 2 > 4 > 3 all parameters as shown in Tables 3 and 4.

Table 3: DFT calculations of the inhibitors in vacuum medium at the equilibrium geometries.

Comp.	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E_{HOMO-LUMO}$ (eV)	μ (Debye)
2	-8.53613228	-2.5892218	5.94691	13.4775
3	-8.63327912	-2.7086825	5.924597	11.0884
4	-8.6153192	-2.6888177	5.926501	11.2538
5	-8.47055136	-2.5356142	5.934937	13.7552
6	-8.51014482	-2.4806459	6.029499	14.9197
7	-9.04635728	-3.2921078	5.75425	3.7094

Table 4: Quantum chemical parameters for inhibitors in vacuum medium as calculated using DFT method.

Inhib.	IE (eV)	EA (eV)	χ (eV)	η (eV)	S (eV)	ω (eV)
2	8.536132	2.589222	5.562677	2.973455	0.336309	5.203269
3	8.633279	2.708682	5.670981	2.962298	0.337576	5.428222
4	8.615319	2.688818	5.652068	2.963251	0.337467	5.390343
5	8.470551	2.535614	5.503083	2.967469	0.336988	5.102652
6	8.510145	2.480646	5.495395	3.014749	0.331703	5.008604
7	9.046357	3.292108	6.169233	2.877125	0.347569	6.614143

The optimized LUMO and HOMO density distributions for gas-phase molecules are shown in Figure 2. When it comes to electron density, red denotes a high value, while green denotes a low one. A metal surface with a high electron density may give electrons to other surfaces. The Green area is where electrons from the metal surface are caught [25]. As a consequence, it is necessary to

consider the distribution of these two areas. Since all of the atoms' nonbonding electrons were in the N=N configuration, the electron density around the receptor was extremely dense. Inhibitor 4, on the other hand, is located in resonance areas and donates N to receptors on the C=O side of the molecule. Although Inhibitor 5 has a high electron density aromatic ring and double bond region, the receptor site is often aromatic and based on double bonds. Similarly.

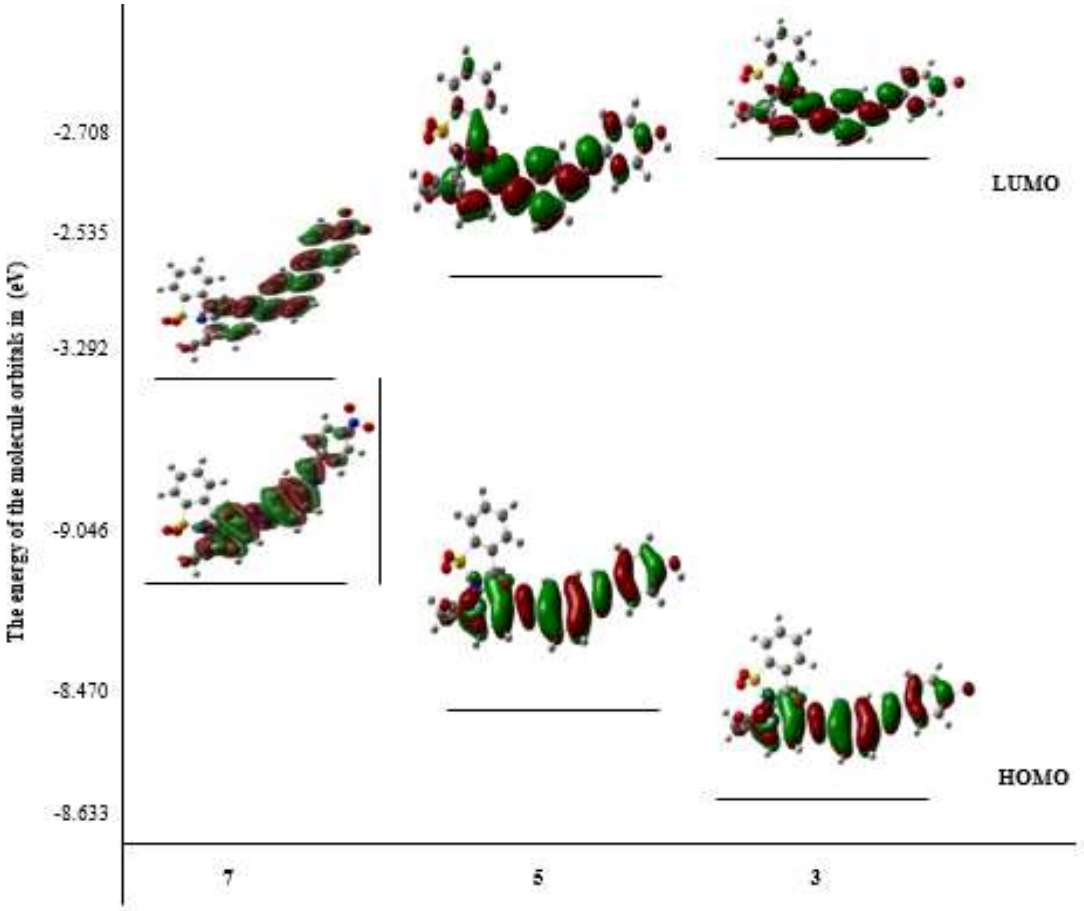
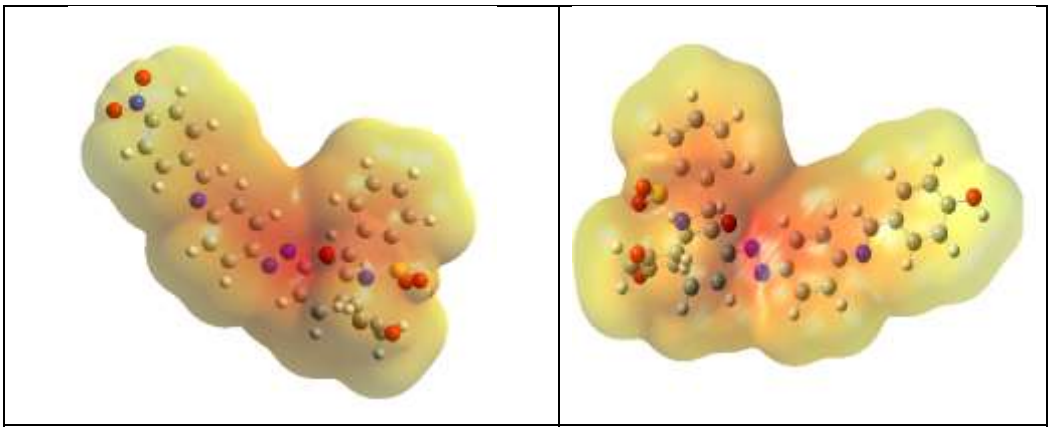


Figure 2: The energy levels (HOMO-LUMO) orbitals of the studied inhibitors (7, 5, and 3).

TED Maps

The electron density of the donor atom dictates the strength of the adsorption link. In other words, the total electron density (TED) of a molecule is a measure of the number of electrons present. As shown in Figure 3, red indicates areas of investigated molecules with a high degree of electron negativity, such as the (O) atom and certain portions of the (NO2), which may aid in the electrophilic attack. These atoms have a yellow hue and are also significantly electronegative [26, 27].



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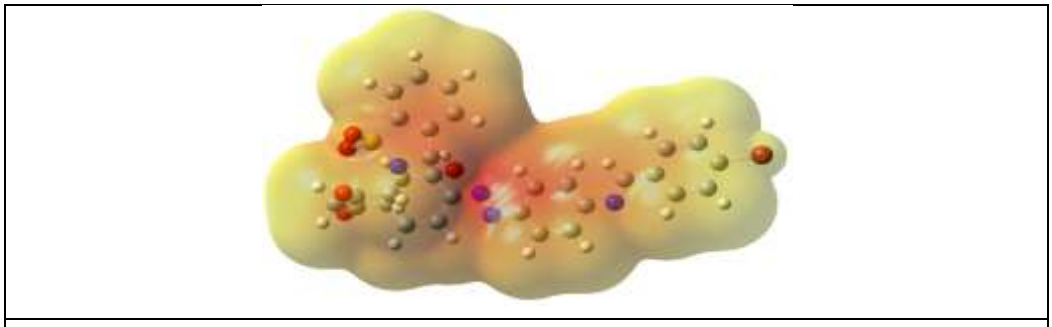

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Figure 3: TED maps of the inhibitors.

4. Conclusions

Computer modeling was utilized to show the corrosive's inhibitory effectiveness. The inhibitors are listed in the following order: 7 > 5 > 2. According to theoretical research, some compounds may be helpful as corrosion inhibitors.

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