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A THEORETICAL APPROACH TO THE INHIBITIVE EFFECT OF TWO NEW SCHIFF BASE COMPOUNDS

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ABSTRACT. The corrosion inhibition of mild steel was investigated using theoretical calculations in 2,2-[2,2-{2-hydroxypropane-1,3diyl}bis(oxy)bis(2,1-phenylene)]bis(methane-l-yl-l-ylidene)bis(azan-l-yl-l-ylidene)diphenol (DF1) and 2,2-[2,2-{ethane-1,2diylbis(oxy)}bis(2,1-phenylene)]bis(methane-l-yl-l ylidene)bis(azan-l-yl-l-ylidene)diphenol (DF2). Various quantum chemical descriptors like E_{HOMO}, E_{LUMO}, ΔE, chemical hardness were calculated and discussed.

1. INTRODUCTION

Corrosion is a natural environmental process for metals and alloys through chemical or electrochemical means. Corrosion leads to huge economic problems in industrial applications [1], the most important ones being acid pickling of steel, chemical cleaning, acid descaling, and oil well acidizing. Corrosion prevention is important in that it measures and gives way to procedures that are aimed at the avoidance of corrosion damages [2]. Methods of corrosion protection are cathodic protection, anodic protection, coating, and alloying. But the most effective and economical method is the application of chemical inhibitors [3–7]. The importance of corrosion inhibitors has two reasons. Firstly it is more economic than the other methods. The second of all protection is connected basically to metal assets, the world's supply of which is restricted. Organic compounds and their derivatives usually serve as inhibitors due to steric factors, heteroatoms, and functional groups that include

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Keywords. Quantum chemical calculations, DFT, electrochemical impedance spectroscopy (EIS), mild steel, adsorption

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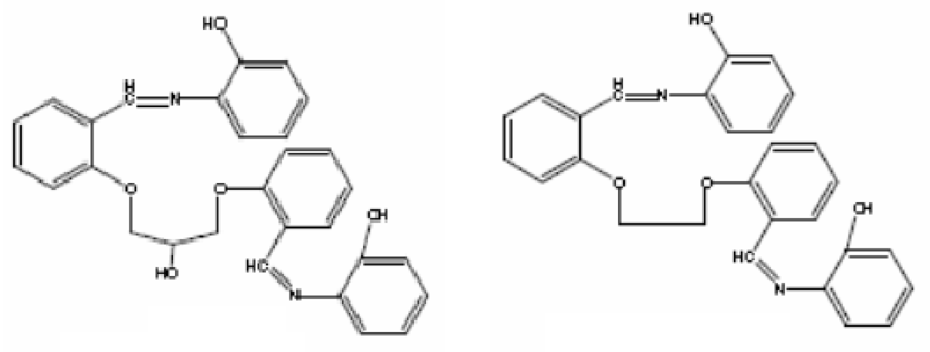
the presence of lonepair of electrons pi bonds of aromatic groups. These inhibitors' efficiency results from forming a protection film on the metal surface are mainly based on adsorption and depend on their chemical/electronic structure [8]. Schiff bases are used in a lot of systems in industrial fields in the form of corrosion inhibitors. They are the reaction products of amine and carbonyl compounds that can be synthesized easily by simple chemical reactions. Recent publications show that Schiff bases act as efficient corrosion inhibitors for various metals like steel, aluminum, and copper in acidic solutions especially HCl [9–13].

Recently, theoretical chemistry has been used to define and understand the mechanism of inhibitor molecules and clarify their properties. Because the experimental methods are costly and take a longtime, theoretical calculations are preferred. Also, experimental methods like, weight loss assessment, electrochemical potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) are often inadequate in explaining inhibition mechanisms [14]. Quantum chemical methods on the other hand have been used to explain, the molecular structure, electron distribution, and the adsorption between inhibitor molecules and metal surfaces. The use of quantum chemical methods presentsan advantage for the characterization of organic inhibitors and substituents based on their molecular structure only in addition to the determination of a large number of molecular properties and characters, like reactivity, shape, and so forth [15,16]. Especially, it is important to calculate quantum chemical parameters, that provide significant contributions to the assessment of inhibition performance, linked to their frontier molecular orbitals (MO) including, [17] the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap (ΔE), ionization potential (I), electron affinity (A), electronegativity (X), global hardness (η), global softness (σ), the transfer of electrons from the surface of the metal tothe inhibitor molecule (ΔEbackdonation), dipole moment (μ), fraction of electron transfers from inhibitor to a metal surface (ΔN) and electrophilicity (ω).

A lot of quantum chemical methods have been in order to investigate corrosion inhibition, such as ab initio Hartree-Fock methods (HF) and the most common type Restricted Hartree-Fock methods (RHF). It is known that the most effective theoretical method is Density Functional Theory, (DFT) the fundamental parameter being electron density. It has been reported that DFT is more advantageous than the other methods because it is simpler than classical quantum mechanics and huge molecules have got many atoms are stimulated regularly [18].

We have used two Schiff bases, 2,2-[2,2-{2-hydroxypropane-1,3diyl}bis(oxy)bis(2,1-phenylene)]bis(methane-1-yl-1-ylidene)bis(azan-1- yl-1-ylidene)diphenol (DF1) and 2,2-[2,2-{ethane-1,2diylbis(oxy)}bis(2,1-phenylene)]bis(methane-1-yl-1-ylidene)bis(azan-1-yl-1-ylidene)diphenol (DF2) synthesized and studied experimentally by H. Derya Leçe [19]. The study showed that DF1 was a better inhibitor than DF2 revealing inhibitor efficiencies of 98±1 and 95±2% in HCl at 303 K. In this paper DF1 and DF2 have been widely studied theoretically from different aspects [19]. Molecular structures of these inhibitors are displayed in Figure 1. The theoretical investigation with quantum chemical calculations using DFT with the B3LYP method with 6-31G basis set was used in determining the molecular structure using Gaussian.



DF1 **DF2**

FIGURE 1. Molecular structure of DF1 and DF2 inhibitors.

2. RESULTS AND DISCUSSION

2.1. Quantum theoretical properties

DF1 and DF2 inhibitor molecules were determined from DFT calculations using B3LYP functional with a 6-31G basis set as implemented in the Gaussian 09 program. B3LYP means including Becke's three-parameter functional (B3) and the gradient corrected correlation functional of Lee, Yang, and Parr (LYP)[20–22].

Frontier molecular orbital theory is an application of the MO theory that focuses on HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) interactions. E_{HOMO} and E_{LUMO} define the electron donating ability and the electron accepting ability, respectively. The energy bandgap (ΔE), is calculated from the E_{HOMO} and E_{LUMO} difference by applying equation 2.1 and is an important aspect for corrosion inhibition [18].

$$\Delta E = E_{LUMO} - E_{HOMO} \tag{2.1}$$

Ionization Potential *(I)* is explained as the total amount of energy that the molecule needs to use to free an electron, which is revolving in the outermost shell of an atom. As Koopmans' theorem explained, the negative value of the highest occupied molecular orbital energy is accepted as the ionization potential. Electron Affinity *(A)* is defined as the energy change that occurs when an electron is added to an atom and is explained as the negative of the lowest unoccupied molecular orbital energy (E_{LUMO}) following Koopman's theorem [23]. Ionization potential and electron affinity are calculated using equations 2.2 and 2.3, respectively.

$$I = -E_{HOMO} \tag{2.2}$$
$$A = -E_{LUMO} \tag{2.3}$$

Electronegativity is the property of an atom that increases with its tendency to attract the electrons of a bond. *I* and *A* are exploited to find the electronegativity of inhibitor molecules by applying equation 2.4, in accordance with the earlier work of Iczkowski and Margrave [24];

$$X = (I+A)/2 = -(E_{LUMO} + E_{HOMO})/2 \tag{2.4}$$

Hardness is fundamentally defined as the resistance of an electronic system to polarization or deformation [25]. According to Janak's theorem and valance state parabola model, global hardness is explained in terms of the relationship between HOMO and LUMO energies of the molecule [26,27]. Global softness is the contrary of global hardness [28]. Equations 2.5 and 2.6 represent global hardness and softness, respectively.

$$\eta = (I-A)/2 = -(E_{LUMO} - E_{HOMO})/2 \tag{2.5}$$
$$\sigma = 1/\eta \tag{2.6}$$

The electron-rich species have been known for several decades as a nucleophile. Otherwise, an electrophile is known to lack the electron. Parr et al. introduced equation 2.7, where ω is named as the "electrophilicity index" that measures the electrophilic power. On the other hand, it can be given in terms of ionization potential and electron affinity, like equation 2.8 [29,30].

$$\omega=\mu^2/2\eta=-X^2/2\eta \tag{2.7}$$

$$\omega=(I+A)^2/8(I+A) \tag{2.8}$$

The dipole moment (μ) is used for expressing the polarity of a molecule. Unfortunately, there is no consensus on its effect on efficiency calculations. It has been reported to increase as well as decrease with changing inhibitor efficiency [18].

The fraction of electrons, ΔN indicates the capability of the investigated inhibitor to pass its electrons to a metal surface or the ability of the tested inhibitor to transfer its electrons to a metal surface. According to Pearson, the value of ΔN can be computed using Eq. 2.9 [31], where X_{Fe} and X_{inh} denote the absolute electronegativity of iron and the inhibitor molecule; η_{Fe} and η_{inh} indicate the absolute hardness of iron and the inhibitor molecule, respectively [32]. The theoretical values of electronegativity and hardness used for iron were 7.0 eV/mol and 0.00 eV/mol, respectively.

$$\Delta N=(\chi_{Fe}-\chi_{inh}) / 2(\eta_{Fe}+\eta_{inh}) \tag{2.9}$$

Back donation of charges is the most favorable situation when a molecule receives a certain number of charges located in some center, it donates the charges back either through the same center or through another one [18]. It is calculated using equation 2.10.

$$\Delta E\mathit{backdonation}=-\eta/4 \tag{2.10}$$

2.2. Quantum theoretical calculations

Inhibition efficiency with DF1 and DF2 inhibitor molecules and their protonated forms have been studied in the aqueous phase. These molecules were calculated using DFT with B3LYP/631G(d,p) model in the water phase. Quantum chemical parameters [33], the energies of the highest occupied molecular orbital (E_{HOMO}), the energies of the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap ΔE, ionization potential *(I),* electron affinity *(A),* electronegativity *(X),* global hardness (η), global softness (σ), ΔEbackdonation, the fraction of electron transfers from inhibitor to a metal surface (ΔN), dipole moment (μ) and electrophilicity (ω) were presented in Table 1.

TABLE 1. Quantum chemical parameters for inhibitor molecules (DF1 and DF2) and their protonated forms ($DF1H^+$ and $DF2H^+$)

Schiff base	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**ΔE (eV)**	***I* (eV)**	***A* (eV)**	**χ (eV)**	**η (eV)**	**σ (eV)**	**ΔE_{BD} (eV)**	**ΔN**	**μ (D)**	**ω**
DF1	-5,689	-1,714	3,975	5,689	1,714	3,702	1,987	0,503	0,497	0,830	8,255	3,447
DF2	-5,647	-1,703	3,944	5,647	1,703	3,675	1,972	0,507	-0,493	0,843	9,521	3,424
$DF1H^+$	-5,707	-3,053	2,654	5,707	3,053	4,380	1,327	0,754	-0,332	0,987	23,877	7,229
$DF2H^+$	-5,753	-3,021	2,732	5,753	3,021	4,387	1,366	0,732	-0,341	0,956	20,904	7,045

Frontier molecular orbitals and electron distributions are critical to investigate the adsorption ability of inhibitor molecules. HOMO and LUMO energies also explain the donor-acceptor electron interaction between the inhibitor and the metal surface [34]. Optimized geometric structure, HOMO, and LUMO electron distributions of neutral and protonated forms of DF1 and DF2 molecules are given in Figure 2 and Figure 3 respectively. When the HOMO electron distribution diagram is examined, it is observed that electron densities are concentrated on heteroatoms and phenyl rings. For protonated molecules, it was concluded that the HOMO electron density was concentrated to the second phenyl ring. It is observed that the LUMO electron diagrams are similar in the neutral and protonated structures.

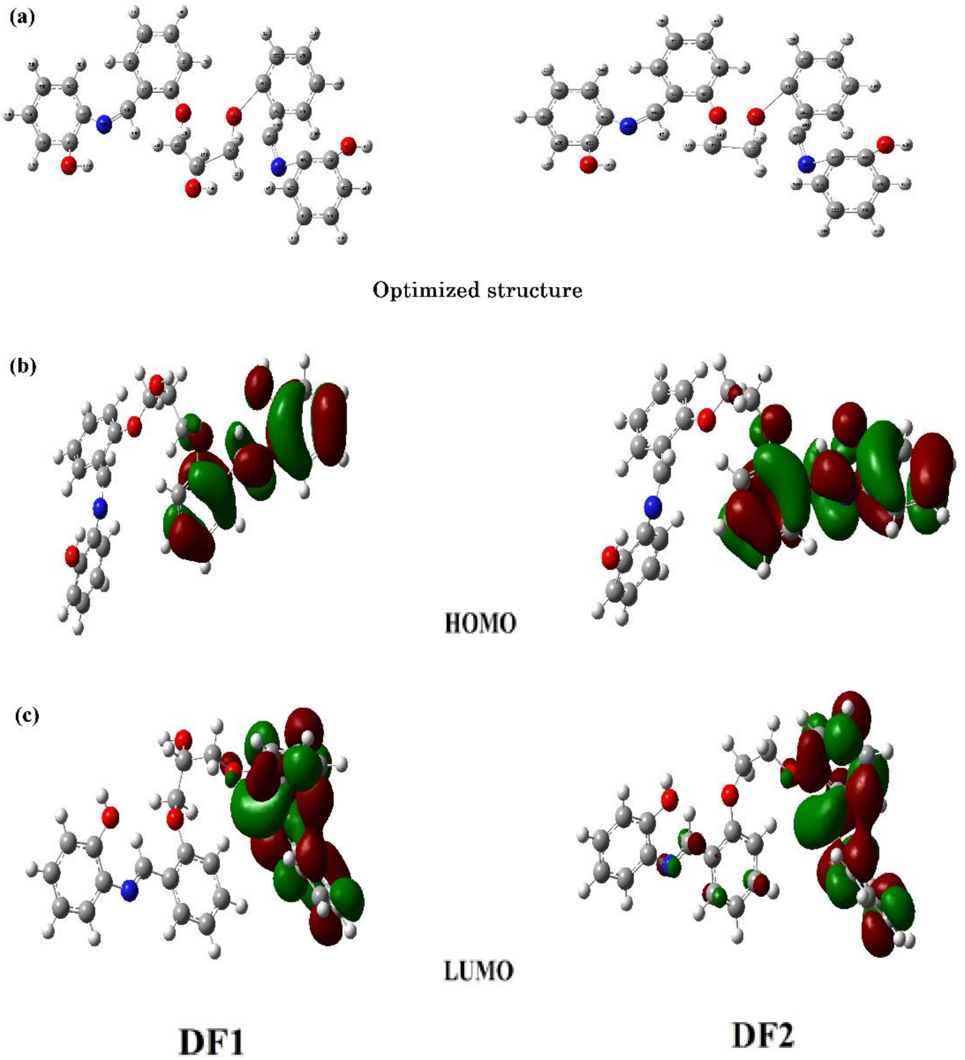


FIGURE 2. (a) Optimized structure, (b) HOMO and (c) LUMO neutral forms of DF1 and DF2 inhibitors molecules.

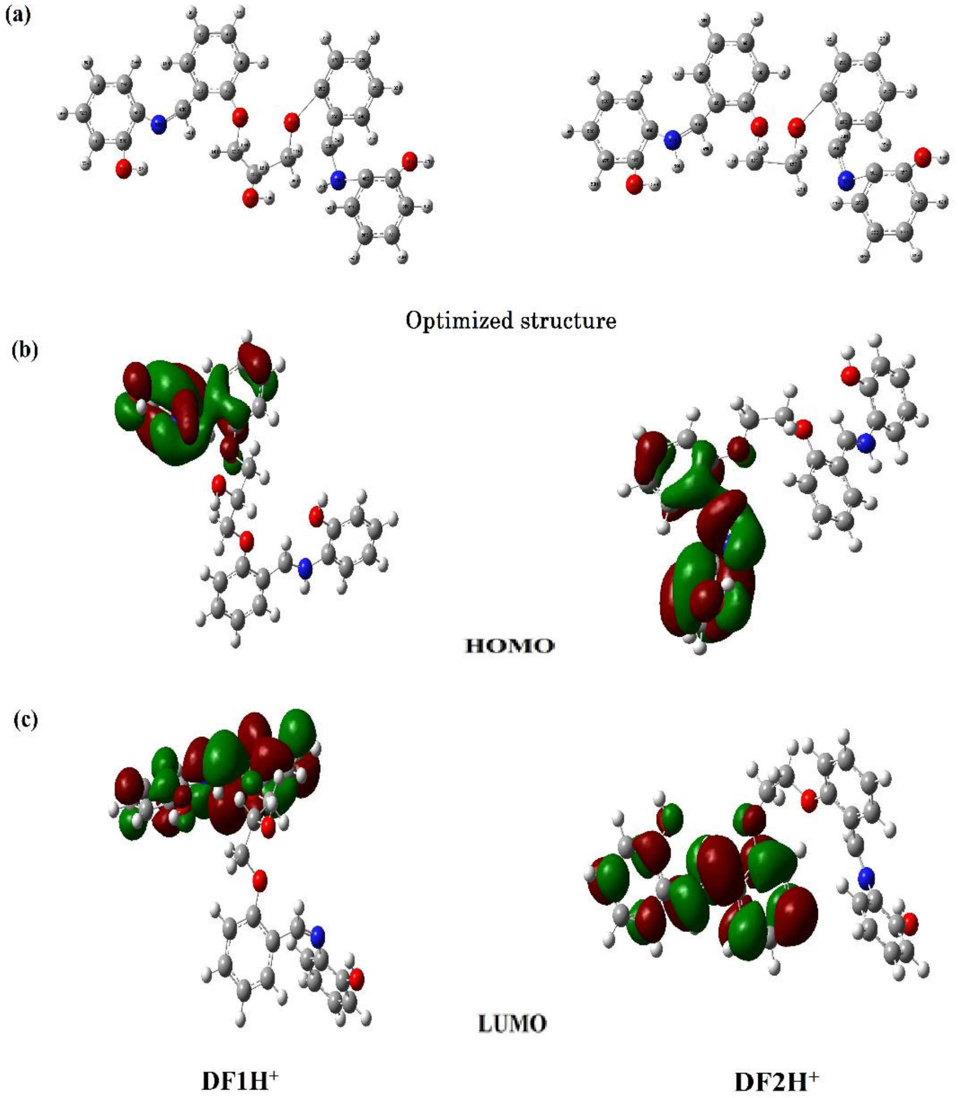


FIGURE 3.(a) Optimized structure, (b) HOMO, and (c) LUMO protonated forms of DF1 and DF2 inhibitors molecules.

When the results are examined, it is observed that the E_{HOMO} values of the neutral molecules (-5,689 and -5,647) are larger than the E_{HOMO} values of the protonated molecules (-5,707 and -5,753). When the E_{LUMO} values are compared, the results are similar[17].

One of the most important parameters for understanding the inhibition efficiency is the ΔE values. If ΔE increases, it affects the reactivity of the chemical species in a way that the reactivity decreases. In this sense, a decrease in ΔE leads to an increase in reactivity. Furthermore, an increase in the reactivity also leads to an increase in the adsorption strength and thus in the inhibition efficiency [32]. When the ΔE values in Table 1 were examined, it is observed that the ΔE values decrease as a result of the protonation of the molecules. It is understood that protonated molecules show better inhibition characteristics due to higher adsorption capabilities related to the charge distribution. When the protonated DF1 and DF2 molecules were compared, it was concluded that the ΔE value of the DF1 molecule (2,654 eV), has the highest reactivity and inhibition efficiency compared to other inhibitors, since the ΔE value was in the lowest energy range.

ΔN values indicate inhibition efficiency caused by electron transfer to the metal surface [35]. Thus, a positive ΔN value indicates that the transfer of electrons from the inhibitor to the metal is high, and a negative value of ΔN value is low. In addition, Lukovis et al. [36] stated that when ΔN values are less than 3.6, inhibitor efficiency increases due to the increase in the ability to absorb electrons on the metal surface. When the ΔN values of the DF1 and DF2 molecules are examined, it is observed that all results are greater than 0 and small than 3.6. Therefore, it can be said that both DF1 and DF2 serve the metal surface as an electron donor and bridge between the inhibitor and the metal surface. Thus, it was concluded that an adsorption layer formed between the inhibitor and the metal prevents corrosion which indicated chemical adsorption. Therefore, it is stated that increased ΔN values result in an increased inhibition effect. Accordingly, the ΔN values (0.987 and 0.956, respectively) of protonated DF1 and DF2 molecules were found to be greater than their neutral states. Moreover, protonated DF1 molecule has a tendency to transfer more electrons and a higher inhibition efficiency, in comparison to the DF2 molecule (Table 1).

Electronegativity, one of the important molecular properties for the determination of inhibition, has been successfully calculated with DFT. Since electronegativity is the capability of attracting electrons in a molecule, the high electronegativity of the molecule attracts the electron more strongly from the metal surface [37]. Thus, it is known that as the electronegativity increases, the inhibition efficiency increases. It was observed that protonated DF1 and DF2 inhibitors exhibited better inhibitory performance due to their greater electronegativity than their neutral states. Table 1 showed that there was little difference in electronegativity between protonated DF1 and DF2 molecules (4,380 eV and 4,387 eV, respectively).

When the literature is examined, it is understood that there is a positive and negative relationship between dipole moment and inhibition performance. However, scientists have often stated that the greater the dipole moment the greater the efficiency of inhibition [38,39],since the physical interaction between the inhibitor and the metal surface is known [40]. Therefore, a positive relationship between the dipole moment of inhibitor and inhibition activity supports physical adsorption. In this study, it is observed that protonated molecules have higher dipoles than neutral molecules. Protonated molecules are susceptible to better inhibition. The dipole moment of protonated DF1 and DF2 molecules were found to be 23,877 Debye and 20,904 Debye, respectively as depicted in Table 1. It was concluded that the protonated DF1 molecule has the best inhibitory performance because of its dipole moment.

According to the hard-soft-acid-base theory (HSAB), Lewis acids and bases are explained in the manner that hard and soft molecules, indicating that hard acids affect hard bases and likely soft bases with soft acids. In addition, it is known that hard molecules are of higher ΔE value, whereas soft molecules are of smaller ΔE value [41]. Metal atoms are thought to be soft acids and inhibitory molecules are soft bases [42]. Soft molecules can be said to be more reactive than hard molecules because of the ability of a soft molecule to easily present electrons to an acceptor. This relationship is explained by the Maximum Hardness Principle, which is expressed as a rule of nature in which molecules regulate themselves [43]. Therefore, inhibitor molecules with lower hardness and higher softness values will interact with the metal surface and adsorb. Thus, soft base inhibitors are said to be more effective for metal corrosion inhibition. In Table 1, it is clear that protonated inhibitors are more effective corrosion inhibition because of their low hardness and high softness. In addition, the protonated DF1 molecule has the lowest hardness (1,327 eV) and the highest softness (0,754 eV) so, it is found that it exhibited the best inhibition, among the inhibitors studied.

The electrophilicity of a chemical species measures the tendency of an atom or molecule to receive electrons. Electron's capacity for electron absorption increases as the ω value increases [44]. Hence, the higher ω value makes it a good electrophile [45]. Table 1 shows the ω values of protonated inhibitor molecules are higher than their neutral state. The ω value of the protonated DF1 inhibitor, 7.229

has the highest electrophilicity. It confirms the protonated DF1 molecule's ability to attract electrons and is a good inhibitor.

Absorption centers of inhibitor molecules can be widely examined via Mulliken charges. This is used to explain the donor-acceptor electron association between DF1, DF2, and metal atoms. It shows that the adsorption ability of negatively charged heteroatoms is better on the metal surface through donor-acceptor interaction [32,46]. Mulliken population investigation was performed in both neutral and protonated forms DF1 and DF2 to analyze their corrosion inhibition activity. Mulliken charges C, O, and N atoms of these inhibitors are listed in Table 2 and Table 3, respectively DF1 and DF2. It is observed that 11O, 22O, 35N, and 50N atoms for DF1 and 11O, 18O, 31N, and 46N atoms for DF2 have the highest negative charge. The most active sites are these atoms that the coordinated covalent bond formed between the electron pairs of negatively charged heteroatoms and the free d orbitals of iron atoms. Thus, it has been proven that the heteroatoms found in the inhibitor molecule are the main adsorption centers on the metal surface.

TABLE 2. Mulliken charges of DF1 inhibitor molecule for neutral and protonated forms

Atoms	**DF1**	**DF1H$^+$**	**Atoms**	**DF1**	**DF1H$^+$**
1C	0.147	0.017	33C	0.177	0.427
2C	0.311	0.325	35N	-0.506	-0.243
3C	-0.034	-0.017	36C	-0.120	0.021
4C	0.037	0.011	37C	-0.025	0.041
5C	-0.030	0.004	38C	-0.172	-0.007
6C	-0.014	0.002	39C	0.315	0.354
11O	-0.469	-0.540	40C	-0.106	0.304
12C	0433	0.319	41C	0.198	0.005
15C	0.214	0.230	46O	-0.019	-0.209
17O	0.229	-0.224	48C	0.063	0.209
19C	0.318	0.320	50N	-0.621	-0.531
22O	-0.493	-0.541	51C	0.022	-0.025
23C	0.103	0.013	52C	0.142	0.296
24C	-0.062	0.021	53C	0.328	0.220
25C	-0.017	0.035	54C	-0.022	0.001
26C	-0.013	0.058	55C	-0.024	-0.021
27C	-0.089	0.013	56C	-0.026	-0.004
28C	-0.042	0.369	61O	-0.133	-0.250

TABLE 3. Mulliken charges of DF2 inhibitor molecule for neutral and protonated forms

Atoms	**DF2**	**DF2H$^+$**	**Atoms**	**DF2**	**DF2H$^+$**
1C	0.014	0.014	31N	-0.538	-0.242
2C	0.327	0.327	32C	-0.013	0.020
3C	-0.018	-0.016	33C	0.000	0.040
4C	0.011	0.012	34C	-0.042	-0.007
5C	0.004	0.007	35C	0.312	0.352
6C	0.004	0.005	36C	0.235	0.303
11O	-0.539	-0.542	37C	-0.028	0.005
12C	0.310	0.325	42O	-0.230	-0.207
15C	0.291	0.311	44C	0.209	0.208
18O	-0.545	-0.535	46N	-0.528	-0.528
19C	0.020	0.011	47C	-0.025	-0.024
20C	-0.020	0.018	48C	0.297	0.297
21C	-0.003	0.033	49C	0.219	0.220
22C	0.001	0.052	50C	0.004	0.005
23C	-0.010	0.026	51C	-0.022	-0.021
24C	0.307	0.358	52C	-0.003	-0.002
29C	0.247	0.425	57O	-0.250	-0.249

3. CONCLUSION

1. The E_{HOMO} values of the neutral forms of DF1 and DF2 (-5,689 and -5.647) are higher in value than those of the protonated forms (-5,707 and -5,753 eV). This indicates the electron donating ability of the neutral form to be higher than that of the protonated form. The E_{LUMO} value of the neutral structures of DF1 and DF2 (-1.714 and -1,703 eV) on the other hand, are larger than the E_{LUMO} value of the protonated forms (-3.053 and -3,021 eV) denoting the protonated structure to have a higher tendency to accept electrons.

2. The protonated forms of the molecules have lower energy gaps, lower hardness, and highest softness values indicating the protonated forms show higher inhibition capabilities. DF1 with its lower energy gap reveals its higher inhibition capability.

3. The protonated form has a higher ω compared to the neutral form indicating the neutral forms behave like a nucleophile, while the protonated forms show electrophilic character.The ω value of the protonated DF1 inhibitor, 7.229 has the highest electrophilicity. It confirms the protonated DF1 molecule's ability to attract electrons and perform as a better inhibitor.

4. The heteroatoms found in the inhibitor molecule are the main adsorption centers on the metal surface.

5. The protonated DF1 molecule tends to transfer more electrons resulting in a higher inhibition efficiency, in comparison to the DF2 molecule.

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Author Contribution Statement Burçin Çakır—Planning, execution, analysis, calculation, interpretation, writing, editing. Kaan C. Emregül—Planning, interpretation, review, editing. All authors discussed the results and contributed to the final manuscript.

Declaration of Competing Interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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