Substituents effects on the corrosion inhibition performance of pyrazolone against carbon steels: quantum chemical and Monte Carlo simulation studies

S. Hadisaputra,¹ * A.A. Purwoko¹ and S. Hamdiani²

¹Chemistry Education Division, University of Mataram, Jalan Majapahit 62, Mataram, 83125, Indonesia

²Department of Applied Chemistry, Chaoyang University of Technology, No. 168, Jifeng E. Rd., Wufeng District, Taichung 41349, Taiwan

*E-mail: rizal@unram.ac.id

Abstract

A quantum chemical and Monte Carlo simulation study on substituents' effect on the corrosion inhibition performance of pyrazolone derivatives has been carried out in gas and aqueous phases. Previously, experimental tests of the corrosion inhibition performance of targeted pyrazolone derivatives have been published. However, the experimental study has not explained the mechanism of inhibition of corrosion on metal surfaces. Density functional theory, *ab initio* MP2 and Monte Carlo simulation are applied as a bridge to understanding the corrosion inhibition mechanism. The interaction patterns and corrosion inhibition mechanisms of pyrazolone derivatives were described using the inhibitor, quantum chemical parameters, Fukui function, and natural bond orbital analysis in the neutral and protonated inhibitor states. A good correlation between the experiment's corrosion inhibition results and the theoretical adsorption energy was obtained and the second-order interaction energy from NBO analysis. The results of the theoretical study are in line with previously published experimental studies. The theoretical research is expected to bridge the gap in designing an effective corrosion inhibitor.

Keywords: DFT, *ab initio*, corrosion inhibition, pyrazolone, Monte Carlo simulation.

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1. Introduction

Corrosion is a problem that is detrimental to the industry. In the oil industry, for example, corrosion causes damage to metal pipelines [1]. Carbon steel is a metal material widely used in industry because it is much cheaper and has been modified to resist corrosion. However, protective carbon steel needs to be done to prevent the effects of corrosion [2]. Efforts to prevent corrosion on carbon steel are the addition of organic inhibitors. It is the most widely used inhibitor to inhibit various metals' corrosion because it is environmentally friendly [3]. The advantage of organic inhibitors is that they have heteroatoms of N, O, S, and P with high electronic density to be firmly attached to metal surfaces [4]. These factors form a thin film on the metal surface, which will inhibit the corrosion rate [5–7]. Many experimental studies

on the inhibition efficiency of organic inhibitor corrosion have been reported [8–10]. The addition of substituents to organic corrosion inhibitors such as OH, OCH₃, CH₃, and NH₂ can increase corrosion inhibition efficiency [11, 12].

Pyrazolone is a 5-membered heterocyclic compound containing two nitrogen atoms and an adjacent carbonyl group (C=O) (Figure 1) [10]. Pyrazolone can be used as an organic corrosion inhibitor. Cao *et al.* studied the corrosion inhibition ability of 1-phenyl-3-methyl-5-pyrazolone in mild steel in 1 M HCl solution. The derivative of pyrazolone was able to inhibit corrosion up to 97.2% [13]. Zhang *et al.* also studied the corrosion inhibition performance of a pyrazolone derivative, namely 1-phenyl-3-amine-5-pyrazolone on carbon steel in H₂SO₄ solution, and obtained an increase in the value of corrosion inhibition efficiency to 98.4% [14]. Furthermore, the effect of substituents on pyrazolone derivatives on inhibition efficiency has been reported by Fouda *et al.* It was shown that the substituent OCH₃ was more effective at inhibiting corrosion than substituents such as CH₃ and NO₂ [15].

Figure 1. 2D and 3D structure of 5-methyl-4-(phenyldiazenyl)-2,4-dihydro-3H-pyrazol-3-one, where: R=H, CH₃, OCH₃ and NO₂.

Fouda *et al.* [15], using weight loss and galvanostatic polarization methods, studied substituents' effect on the corrosion inhibition of pyrazolone derivatives against carbon steel. However, this experimental study has limitations, namely that it has not yet explained in detail the mechanism of inhibition by inhibitors on the metal surface. Theoretical studies have proven to provide solutions to similar problems before, in particular on corrosion inhibition. Theoretical research using the density functional theory approach and *ab initio* can describe the structural properties and inhibition mechanism well [16–18]. Furthermore, molecular dynamics simulations can explain the influence of orientation and structure on the inhibitor interaction pattern on metal surfaces [19, 20]. This research will focus on a combination of density functional theory, *ab initio*, and Monte Carlo simulation to explain the interaction mechanism between pyrazolone derivatives and metal surfaces in quantum parameters, Fukui function, and NBO analysis and test the substituent effects on the corrosion performance.

2. Methodology

Quantum chemical calculation

Theoretical studies based on DFT/B3LYP and *ab initio* MP2 were carried out at the theoretical level 6–311++G(d, p). DFT was adopted to simulate the molecular properties, reactivity, and selectivity of organic molecules quickly and cheaply [19]. The *ab initio* method was chosen because it can measure quantum parameters more accurately than DFT [20]. All quantum chemical calculations use Gaussian software 09 [21]. The inhibitor's quantum parameters are the highest occupied molecular orbital HOMO, lowest unoccupied molecular orbital LUMO, ionization potential I , electron affinity A , electronegativity χ , hardness η , electron transfer value ΔN . The ionization potential I and the electron affinity A were calculated using the theorem of Koopman [22]. Koopman's theorem is applied to explain the relationship between ionization potential I and electron affinity A with energy levels (HOMO and LUMO energies) according to equations 1 and 2.

$$I = -E_{\text{HOMO}} \quad (1)$$

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

Electronegativity (χ) is the power of an atom or a group of atoms to attract electrons to itself [23], this can be calculated by equation 3:

$$\chi = \frac{I + A}{2} \quad (3)$$

Hardness (η) can be calculated based on equation (4) as follows [24, 25]:

$$\eta = \frac{I - A}{2} \quad (4)$$

Analyze the function of Fukui as the active site in the inhibitor, to determine its reactivity [26]. The analysis of the Fukui function can be calculated using equations 5 and 6:

$$f^+(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)}^+ = \rho_{N+1}(r) - \rho_N(r) \quad (5)$$

$$f^-(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)}^- = \rho_N(r) - \rho_{N-1}(r) \quad (6)$$

where $\rho_{N+1}(r)$, $\rho_N(r)$ and $\rho_{N-1}(r)$ are the electronic density at point r for a system with $N+1$, N and $N-1$ electrons, respectively. $f^+(r)$ can be associated with reactivity for nucleophilic attack. It can measure the intramolecular reactivity on the active site of r towards the nucleophilic reagent. $f^-(r)$ is associated with reactivity for electrophilic attack and thus serves to measure the intramolecular reactivity in the active site r towards electrophilic reagent [26].

According to the Pearson theory [27, 28], the value of ΔN electron transfer from organic molecules to metals can be calculated by equation 7:

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})}, \quad (7)$$

where χ_{Fe} and χ_{inh} donate the absolute electronegativity of Fe metal and organic inhibitor molecules while η_{Fe} and η_{inh} are the absolute hardness of iron and organic inhibitor molecules. Therefore, for the theoretical values $\chi_{\text{Fe}}=7.0$ eV and $\eta_{\text{Fe}}=0$ eV to calculate the number of electrons transferred [28, 29].

Electron delocalization interactions can be seen quantitatively using the stabilization energy (E^2), which can be estimated based on the theory of “The second-order perturbation.” Stabilization energy can be formulated by equation 8:

$$E^2 = \Delta E_{i,j} = q_i \frac{F^2}{E_i - E_j}, \quad (8)$$

where E^2 is the stabilization energy, q_i denotes the donor orbitals' location, E_i and E_j are the donor and acceptor energies of NBO, and F_{ij} is the Fock matrix elements between the orbitals of NBO i and j [30, 31].

Monte Carlo simulation

The organic inhibitor adsorption of pyrazolone derivatives with the addition of substituents on the carbon steel surface was theoretically modeled using the Monte Carlo (MC) simulation approach. Monte Carlo simulation of pyrazolone derivatives with the addition of substituents from 100 water molecules using Material Studio 7.0 [32]. Optimization is done with the forcite module using the COMPASS force field. The surface of carbon steel can be represented by the Fe(110) plane, which has been done before because the Fe(110) crystalline plane is the most stable and has a moderate Fe atomic density [33]. The Fe(110) field is then enlarged to become a supercell (8×8). After that, a vacuum plate with a thickness of 8.0 nm was built up in the Fe(110) plane. The adsorption energy (E_{ads}) of the most stable conformation of the inhibitor/Fe(110) is obtained in the neutral and protonated state of each pyrazolone derivative compound with the addition of substituents (H, CH₃, OCH₃, and NO₂).

3. Results and Discussion

As a consequence of choosing the DFT and *ab initio* methods, the accuracy of calculations must be validated by comparing theoretical and experimental calculations. The comparison of the pyrazolone crystal structure published previously with the results of theoretical studies [34] can be seen in Table 1. Table 1 shows the pyrazolone derivatives' geometrical parameters calculated using DFT and *ab initio* MP2 based on 6–311++G(d, p) level of theory. A reasonably low difference between experimental and theoretical studies was obtained, the difference from the bond distance was obtained at 0.03327 Å, and the bond

angle obtained 2.4598° . It shows that the two methods with the theoretical level can be appropriately used to explain the compounds studied.

Table 1. Comparison of the crystal structure of experimental pyrazolone derivatives [34] vs. theoretical B3LYP/6–311++G(d, p).

Bond	Exp [34]	Theory	Bond angle	Exp [34]	Theory
N1–N2	1.407	1.3918	N2–C9–C11	114.9	112.7294
N2–C9	1.284	1.2883	C9–C11–C12	104.5	100.9127
C9–C10	1.487	1.4911	N1–C12–C11	99.7	103.2395
C9–C11	1.482	1.5175	N1–N2–C9	107.2	107.7422
C11–C12	1.540	1.5550			
N1–C12	1.501	1.3755			

The quantum chemical parameters show that the presence of heteroatoms (N, O) and π bonds in pyrazolone derivatives increases their corrosion inhibition performance against carbon steel. Quantum chemical parameters can be used to determine pyrazolone's theoretical chemical properties so that quantum parameters can be used to predict the corrosion inhibition efficiency of pyrazolone derivatives. The addition of substituents (CH_3 , OCH_3 , and NO_2) affect the value of corrosion inhibition efficiency [15]. As a consequence of the inhibitor's application to the acid medium, apart from the neutral molecule's electronic properties, the electronic properties of the protonated form of the inhibitor were also investigated. The electron-rich sites of inhibitors such as oxygen, nitrogen, and carbon atoms sharing multiple bonds become protonated. The most likely protonated sites are found based on the protonation affinity and basicity. The quantum chemical parameters (such as HOMO energy level, ionization potential, electronegativity, and electron transfer), neutral and protonated inhibitors are shown in Tables 2–5.

HOMO energy shows the ease of the nature of the molecule to donate its electrons; the greater the energy value of the HOMO, the stronger the inhibitor is to adhere to the metal surface so that it can increase the efficiency of corrosion inhibition [24]. The high energy level of HOMO in the inhibitor can more easily donate its lone pair and π bonds to iron atoms to interact to form complex compounds [24]. In general (Table 2–5), the highest HOMO energy level value of the pyrazolone derivative was obtained for the OCH_3 substituent of -8.7060 eV, higher than the other substituents (H, CH_3 , and NO_2). The order of the HOMO energy levels is $\text{OCH}_3 > \text{CH}_3 > \text{H} > \text{NO}_2$. The high HOMO energy level on the OCH_3 substituent indicates that the inhibitor readily donates more lone pairs to the ferrous metal to interact to form complexes with the metal surface. The interactions that occur will be stronger and have a good effect on the inhibitory power of corrosion.

Figure 2. The relationship between the inhibition efficiency of pyrazolone derivatives and quantum parameters in the neutral form.

Figure 3. The relationship between the inhibition efficiency of pyrazolone derivatives and quantum parameters in the protonated form.

Table 2. The quantum chemical parameters of pyrazolone derivatives and the effect of the substituent calculated using B3LYP and MP2 with the 6–311++G(d, p) basis set in gas medium.

–R	E_{HOMO}	E_{LUMO}	ΔE	I	A	χ	η	ΔN
H								
B3LYP/6–311++G(d, p)	–6.9092	–2.5505	–4.3587	6.9092	2.5505	4.7299	2.1794	0.5208
MP2/6–311++G(d, p)	–9.2440	0.9804	–10.2244	9.244	–0.9804	4.1318	5.1122	0.2805
CH₃								
B3LYP/6–311++G(d, p)	–6.8099	–2.4338	–4.3761	6.8099	2.4338	4.6219	2.1881	0.5434
MP2/6–311++G(d, p)	–8.9278	0.9595	–9.8873	8.9278	–0.9595	3.9842	4.9436	0.305
OCH₃								
B3LYP/6–311++G(d, p)	–6.472	–2.3353	–4.1367	6.472	2.3353	4.4036	2.0683	0.6276
MP2/6–311++G(d, p)	–8.6211	0.9151	–9.5362	8.6211	–0.9151	3.853	4.7681	0.3300
NO₂								
B3LYP/6–311++G(d, p)	–7.2929	–3.5884	–3.7046	7.2929	3.5884	5.4406	1.8523	0.4209
MP2/6–311++G(d, p)	–10.1637	0.0778	–10.2416	10.1637	–0.0778	5.043	5.1208	0.1911

Table 3. Quantum chemical parameters of neutral pyrazolone derivatives calculated using B3LYP/6–311++G(d, p) and MP2/6–311++G(d, p) in the aqueous medium.

–R	E_{HOMO}	E_{LUMO}	ΔE	I	A	χ	η	ΔN
H								
B3LYP/6–311++G(d, p)	–7.0442	–2.655	–4.3892	7.0442	2.655	4.8496	2.1946	0.4899
MP2/6–311++G(d, p)	–9.287	1.1227	–10.4097	9.287	–1.1227	4.0821	5.2049	0.2803
CH₃								
B3LYP/6–311++G(d, p)	–6.9239	–2.5707	–4.3533	6.9239	2.5707	4.7473	2.1766	0.5175

–R	<i>E</i>_{HOMO}	<i>E</i>_{LUMO}	ΔE	<i>I</i>	<i>A</i>	χ	η	ΔN
MP2/6– 311++G(d, p)	–8.9776	1.0852	–10.0628	8.9776	–1.0852	3.9462	5.0314	0.3035
OCH₃								
B3LYP/6– 311++G(d, p)	–6.5446	–2.5013	–4.0433	6.5446	2.5013	4.5229	2.0217	0.6126
MP2/6– 311++G(d, p)	–8.706	1.0787	–9.7847	8.706	–1.0787	3.8137	4.8923	0.3256
NO₂								
B3LYP/6– 311++G(d, p)	–7.149	–3.5658	–3.5832	7.149	3.5658	5.3574	1.7916	0.4584
MP2/6– 311++G(d, p)	–9.9901	0.1415	–10.1316	9.9901	–0.1415	4.9243	5.0658	0.2049

Table 4. Quantum chemical parameters of protonated pyrazolone derivatives calculated using B3LYP/6–311++G(d, p) and MP2/6–311++G(d, p) in the gas phase.

–R	<i>E</i>_{HOMO}	<i>E</i>_{LUMO}	ΔE	<i>I</i>	<i>A</i>	χ	η	ΔN
Protonated H								
B3LYP/6– 311++G(d, p)	–10.0718	–7.1776	–2.8942	10.0718	7.1776	8.6247	1.4471	–0.5613
MP2/6– 311++G(d, p)	–12.0168	–2.9745	–9.0423	12.0168	2.9745	7.4957	4.5212	–0.0548
Protonated CH₃								
B3LYP/6– 311++G(d, p)	–9.7286	–7.079	–2.6496	9.7286	7.079	8.4038	1.3248	–0.5298
MP2/6– 311++G(d, p)	–11.6225	–2.8953	–8.7272	11.6225	2.8953	7.2589	4.3636	–0.0297
Protonated OCH₃								
B3LYP/6– 311++G(d, p)	–9.21	–6.9901	–2.2199	9.21	6.9901	8.100	1.1100	–0.4955
MP2/6– 311++G(d, p)	–11.2759	–2.8561	–8.4198	11.2759	2.8561	7.066	4.2099	–0.0078
Protonated NO₂								
B3LYP/6– 311++G(d, p)	–10.6609	–7.506	–3.1549	10.6609	7.506	9.0834	1.5774	–0.6604

MP2/6– 311++G(d, p)	–12.8158	–3.3304	–9.4853	12.8158	3.3304	8.0731	4.7427	–0.1131
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Table 5. Quantum chemical parameters of protonated pyrazolone derivatives calculated using B3LYP/6–311++G(d, p) and MP2/6–311++G(d, p) in the aqueous medium.

–R	E_{HOMO}	E_{LUMO}	ΔE	I	A	χ	η	ΔN
Protonated H								
B3LYP/6– 311++G(d, p)	–7.4801	–3.3312	–4.1489	7.4801	3.3312	5.4057	2.0745	0.3843
MP2/6– 311++G(d, p)	–9.5036	0.8523	–10.3558	9.5036	–0.8523	4.3257	5.1779	0.2582
Protonated CH₃								
B3LYP/6– 311++G(d, p)	–7.2029	–3.3054	–3.8975	7.2029	3.3054	5.2541	1.9487	0.448
MP2/6– 311++G(d, p)	–9.1828	0.8969	–10.0796	9.1828	–0.8969	4.1429	5.0398	0.2834
Protonated OCH₃								
B3LYP/6– 311++G(d, p)	–6.7642	–3.2746	–3.4896	6.7642	3.2746	5.0194	1.7448	0.5676
MP2/6– 311++G(d, p)	–8.9036	0.9241	–9.8277	8.9036	–0.9241	3.9897	4.9138	0.3063
Protonated NO₂								
B3LYP/6– 311++G(d, p)	–7.7792	–3.7982	–3.981	7.7792	3.7982	5.7887	1.9905	0.3043
MP2/6– 311++G(d, p)	–10.1934	–0.0634	–10.13	10.1934	0.0634	5.1284	5.065	0.1848

Previous research reported by Fouda *et al.* showed that substituents' presence changed pyrazolone corrosion inhibition efficiency. The OCH₃ substituent addition was more efficient at inhibiting carbon steel corrosion in a hydrochloric acid medium (Figure 4). This substituent increases the nitrogen atoms' electron density due to the mesomeric effect, which facilitates the stronger adsorption of the OCH₃–substituted pyrazole on the carbon steel surface. It may explain why the inhibition efficiency of OCH₃ is higher than that of H, CH₃, and NO₂ [12]. It is consistent with previous reports on NO₂ substituted benzimidazole, which reduced corrosion inhibition efficiency values [12].

The low ionization potential indicates that it is easy for an atom to remove its outer electrons so that it is easy to donate electrons from the molecule to the metal surface. This high electron donor rate increases the efficiency of corrosion inhibition. The high ionization

potential indicates that the electrons do not easily escape from the outer shell, which implies the electron transfer process's difficulty to the surface of the ferrous metal (Fe). This process reduces the efficiency of corrosion inhibition. Table 2–5 shows the lowest ionization potential value of OCH_3 -substituted pyrazolone of 8.7060 eV calculated using B3LYP/6–311++G(d, p). Main-Bobo *et al.* reported that pyrazolone's potential ionization value using photoionization mass spectrometry was 9.25 eV [35]. It shows that B3LYP/6–311++G(d, p) has not approached the experimental results. Thus, the theoretical computations' quality was improved using MP2/6–311++G(d, p). The value of the pyrazolone ionization potential of 9.2870 eV was obtained in the MP2/6–311++G(d, p) method. Even though the values differ, the trend between the two methods still shows that OCH_3 has the greatest influence on corrosion inhibition efficiency. OCH_3 is more reactive to iron and causes a strong interaction between the inhibitor and the metal surface. The strength of this reaction has an impact on the high value of the corrosion inhibition efficiency.

Figure 4. The corrosion inhibition efficiency values of several pyrazolone derivatives in experimental studies [15].

In the interaction between inhibitors and metals, electrons from molecules with low electronegativity will move towards a high electronegativity molecule. The small electronegativity of a molecule makes it easy for the molecule to donate electrons to become more reactive. Conversely, a considerable electronegativity value indicates the molecule to be unreactive [25]. Theoretically, iron metal's electronegativity value (7 eV) is higher than the electronegativity value of pyrazolone derivatives such as OCH_3 , 3.8137 eV, so it tends to release electrons. The electronegativity values can be seen in Table 2–5, which shows that OCH_3 has a high corrosion inhibiting efficiency compared to the pyrazolone substituted CH_3 and NO_2 .

Electron transfer will occur from the inhibitor to the metal surface if ΔN is positive and the value is less than $\Delta N < 3.6$, so that the value of inhibition efficiency is high [36]. An electron-donating group can increase corrosion inhibition efficiency because it can increase electrons' transfer to the metal surface. According to Koopman (1934), the highest electron

transfer value (ΔN) will produce the best inhibitor efficiency [23]. Tables 2–5 show the value of the electron transfer amount of the pyrazolone derivative. The high electron transfer value is again demonstrated by the OCH_3 substituted pyrazolone of 0.3256 eV. These results are consistent with the results of previous experiments reported by Fouda *et al.*

Figure 5 shows the shape of the HOMO and LUMO orbitals, and electrostatic potential (ESP) distribution of the respective inhibitors. Electron rich inhibitors capable of donating electrons to metal surfaces increase their ability to inhibit corrosion in carbon steels [22]. The HOMO orbital can be distributed evenly with the molecule's electrons, whereas the LUMO orbital has an anti-bonding character [23]. The electron density indicates that a negative charge in red is easily delocalized on the N atom because of the lone pair. Figure 5 also shows the molecular ESP inhibitors. ESP is an opportunity to find the distribution of electron charges in coordinates (x , y , and z) in a molecule. ESP is closely related to electron density to explain molecules' properties, predict molecular structure, bond strength, reactivity, and stability. ESP shows the active site of the pyrazolone derivative, which has aromatic and heteroatoms in its structure. Figure 5 shows that the blue and red colors can represent both electron-poor and electron-rich regions. It appears that the active sites of the pyrazolone derivative are aromatic regions and nitrogen heteroatoms.

Fukui function analysis is an index that distinguishes each part of a molecule based on its characteristic properties. Each molecule has a different active site so that the function of Fukui can be used to find a picture of the active site that can be used in interaction. The nucleophilic and electrophilic attacks can be controlled by the maximum values of f^+ and f^- [37, 38]. The greater the Fukui function's value, the more reactive the active side of a molecule is. The f^+ symbol indicates the ability of an inhibitor to accept electrons from a metal surface.

On the other hand, the symbol f^- denotes electrons' donation to the empty orbital in the metal by the inhibitor [39]. Table 6 shows the function of the pyrazolone derivative Fukui. High f^+ values are found in C (1), N (7), and N (8) atoms, so that these atoms are predicted to experience a back donation from the Fe atom. High f^- values are found in C (10), N (8), and O (18) atoms. It shows that the atom donates its electrons to the Fe atom so that coordination covalent bonds occur.

Table 6. Fukui functional analysis of pyrazolone derivatives.

–R	Atom	N–	N	N+	f^+	f^-
H	C1	–0.17461	–0.30409	–0.39428	–0.09019	–0.12948
	C2	–0.18812	–0.12862	–0.11335	0.01526	0.05951
	C3	–0.19955	–0.16665	–0.14560	0.02104	0.03290
	C4	–0.38056	–0.31630	–0.27974	0.03656	0.06426
	C5	–0.35667	–0.31714	–0.28420	0.03294	0.03953
	C6	0.03552	0.15797	0.23052	0.07255	0.12245

–R	Atom	N–	N	N+	<i>f</i>⁺	<i>f</i>[–]
	N7	–0.20155	0.04694	0.18442	0.13748	0.24850
	N8	–0.06986	0.20687	0.39301	0.18614	0.27672
	C9	–0.20037	–0.39309	–0.48249	–0.08940	–0.19272
	C10	0.25742	0.29380	0.34634	0.05254	0.03638
	C11	–0.69783	–0.71997	–0.74721	–0.02724	–0.02214
	N12	–0.14044	–0.09881	0.01321	0.11202	0.04163
	C13	0.12092	0.16179	0.16603	0.00424	0.04088
	O14	–0.45483	–0.40963	–0.28436	0.12527	0.0452
	N15	–0.20628	–0.19289	–0.10544	0.08744	0.0134
CH₃	C1	–0.10492	–0.57179	–0.61237	–0.04057	–0.46687
	C2	0.06551	–0.29437	–0.26023	0.03414	–0.35988
	C3	–0.04023	–0.56967	–0.56151	0.00816	–0.52944
	C4	0.16079	0.56023	0.65367	0.09344	0.39944
	C5	–0.06573	–0.18354	–0.09125	0.09229	–0.11781
	C6	0.26456	0.24128	0.31384	0.07257	–0.02329
	N7	0.24618	0.03546	0.13748	0.10201	–0.21072
	N8	0.46306	0.23330	0.36069	0.12739	–0.22977
	C9	–0.04279	–0.34642	–0.40007	–0.05365	–0.30363
	C10	0.03025	0.27465	0.29227	0.01762	0.24441
	C11	–0.00687	–0.72675	–0.74503	–0.01828	–0.71988
	N12	0.00961	–0.10068	–0.03231	0.06837	–0.11029
	C13	0.03295	0.15893	0.16065	0.00172	0.12598
	O14	0.00230	–0.4104	–0.33127	0.07913	–0.4127
	N15	0.00345	–0.19391	–0.15568	0.03823	–0.19736
	C16	–0.01893	–0.58765	–0.59429	–0.00663	–0.56872
OCH₃	C1	–0.37451	–0.54405	0.33104	0.87509	–0.16955
	C2	0.00310	0.07163	–0.11080	–0.18244	0.06853
	C3	–0.44546	–0.44329	0.13968	0.58298	0.00217
	C4	–0.49963	–0.49621	0.17327	0.66948	0.00342
	C5	0.18397	0.26946	0.09370	–0.17576	0.08549
	C6	–0.01215	0.15326	–0.01428	–0.16754	0.16541
	N7	–0.24030	0.00918	–0.10565	–0.11483	0.24948

–R	Atom	N–	N	N+	<i>f</i>⁺	<i>f</i>[–]
	N8	–0.04855	0.23091	0.18981	–0.04110	0.27946
	C9	–0.14078	–0.32990	–0.00150	0.32841	–0.18912
	C10	0.23252	0.26600	0.00729	–0.25871	0.03348
	C11	–0.69799	–0.72035	0.00248	0.72283	–0.02236
	N12	–0.14405	–0.10245	0.01689	0.11934	0.04159
	C13	0.11617	0.15996	0.00511	–0.15485	0.04379
	O14	–0.45670	–0.41385	0.02874	0.44259	0.04285
	N15	–0.20413	–0.19185	0.01360	0.20544	0.01228
NO₂	C1	–0.44392	–0.49188	0.57678	1.06865	–0.04796
	C2	–0.32929	–0.28346	–0.27102	0.01245	0.04583
	C3	–0.14786	–0.05565	–0.04038	0.01526	0.09221
	C4	–0.33718	–0.49117	–0.51118	–0.02001	–0.15399
	C5	–0.23424	–0.13112	–0.11320	0.01791	0.10312
	C6	0.36895	0.49241	0.55934	0.06693	0.12346
	N7	–0.07025	0.03838	0.12724	0.08886	0.10864
	N8	0.13992	0.28991	0.42870	0.13879	0.14999
	C9	–0.30986	–0.39455	–0.44297	–0.04841	–0.08470
	C10	0.27822	0.29170	0.37272	0.08102	0.01348
	C11	–0.71161	–0.72090	–0.74882	–0.02792	–0.00929
	N12	–0.11630	–0.09287	0.04512	0.13799	0.02342
	C13	0.14292	0.15591	0.14425	–0.01165	0.01299
	O14	–0.42580	–0.39716	–0.22877	0.16839	0.02864
	N15	–0.19785	–0.18943	–0.05462	0.13481	0.00842
	N16	–0.16780	–0.10832	–0.09977	0.00855	0.05949
	O17	–0.22120	–0.05979	–0.04914	0.01065	0.16141
	O18	–0.21573	–0.05387	–0.04285	0.01102	0.16186

Natural Bond Orbital NBO analysis indicates the strength of the interaction between atoms, which involves the amount of charge transfer and affects molecular stability. Analysis of NBO as the second-order interaction energy E^2 can be used to determine the orbital filled with electrons or empty, which contributes to the delocalization of electrons from bonding (BD) or lone pair (LP) to anti-bonding (BD)* [40]. Bonding BD shows the condition of the atom that is bonded to other atoms. The Lone Pair symbol LP shows a lone pair on the

associated atom, and the Rydberg symbol RY indicates the type of atomic orbital with the highest quantum number and energy [41]. Metal atoms and vice versa metal atoms can provide a back donation to the inhibitor. Table 7 shows the E^2 value from the NBO analysis using the DFT method. The order of E^2 values is $\text{OCH}_3 > \text{CH}_3 > \text{H} > \text{NO}_2$. The OCH_3 has the highest E^2 value compared to other substituents, $51.19 \text{ kcal} \cdot \text{mol}^{-1}$, which indicates that the interaction between the electron pair (LP) of the N (8) atom and the Fe (30) atom forms the strongest bond. The N (8) donates electrons to Fe (30); besides, N (8) atoms can also accept electrons from Fe (30) or back donations, but the E^2 back donation value is relatively small. Substituent OCH_3 has the greatest effect on increasing corrosion inhibition efficiency compared to other substituents because it has the highest E^2 .

Table 7. Natural Bonding Orbital NBO analysis of substituted pyrazolone.

–R	Donor(<i>i</i>)	→	Acceptor(<i>j</i>)	E^2 (kcal·mol^{–1})
H	LP(1) N8	→	LP*(3) Fe26	43.24
	LP(1) N15	→	LP*(4) Fe26	21.85
	BD(1) C12–N15	→	LP*(4) Fe26	9.60
	LP*(3) Fe26	→	RY*(10) N8	9.03
	LP*(3) Fe26	→	RY*(3) N15	3.22
CH₃	LP(1) N8	→	LP*(4) Fe29	49.92
	LP(1) N15	→	LP*(5) Fe29	27.61
	BD(1) N12–N15	→	LP*(5) Fe29	10.59
	LP*(4) Fe29	→	RY* (10) N8	8.65
	LP*(4) Fe29	→	RY* (10) N15	3.21
OCH₃	LP(1) N8	→	LP*(4) Fe30	51.19
	LP(1) N15	→	LP*(5) Fe30	28.91
	BD(1) C9–C10	→	LP*(6) Fe30	8.27
	BD(1) N12–N15	→	LP*(5) Fe30	10.50
	LP*(4) Fe30	→	RY*(2) N15	3.30
	LP*(4) Fe30	→	RY*(10) N8	8.93
NO₂	LP(1) C6	→	LP* (3)Fe28	16.01
	LP(1) N8	→	LP* (3)Fe28	31.07
	BD(1) C1–C6	→	LP*(4) Fe28	7.90
	BD(1) C9–C10	→	LP*(5) Fe28	8.74
	LP (2)Fe28	→	RY* (1) C6	8.63
	LP (2)Fe28	→	RY* (11) N8	4.73

Figure 5. Visualization of HOMO, LUMO orbitals, and ESP distribution of pyrazolone derivatives.

The quantum chemical parameters are not sufficient to predict the corrosion inhibition mechanism of the targeted inhibitor. Therefore, it is essential to carry out molecular simulations of the inhibitor interactions with the iron surface in water to mimic actual experimental studies [42]. The interaction between inhibitor and carbon steel can

theoretically be modeled using Monte Carlo simulation, whereas carbon steel can be represented by Fe surface (110) [43] can be seen in Figure 6. Monte Carlo simulation helps find the adsorption site on the metal surface by finding the low energy adsorption site on periodic and non-periodic substrates or by investigating the preferential adsorption of a mixture of adsorbate components [44]. Molecular simulation studies are designed to test the relationship between the inhibitor and the metal surface. The lowest energy configuration value is the most stable adsorption energy of the inhibitor in the Fe(110) / 100H₂O system using Monte Carlo simulations. The analysis results on the shortest bond length of the inhibitor active site bond with ferrous metal measuring less than 3.50 Å, which indicates that the formation of a thin layer of the inhibitor is firmly attached to the Fe surface [45, 46]. Table 8 shows the inhibitor with the OCH₃ substituent giving the maximum adsorption energy during the simulation process. It explains the highest inhibition obtained from the maximum electron-acceptor donation of OCH₃ during its interaction with the metal surface. The empty d-orbitals of Fe tend to fill with electrons. The pyrazolone derivative has several lone pair electrons containing O and N atoms making it possible to supply the unoccupied Fe orbital electrons to form stable coordination bonds. Therefore, the studied molecules tend to adsorb on the Fe surface to create a stable adsorption layer and protect the ferrous metal from corrosion [42]. Figure 7 and show the neutral and protonated adsorption of the pyrazolone derivative on a Fe(110) surface. The correlation between each system's adsorption energy with quantum parameters can be seen in Figures 7 and 8. The higher the adsorption energy, the stronger the adsorption [26]. The results showed that the adsorption energy value had the order OCH₃ > CH₃ > H > NO₂ as well as the protonated molecular concentration OCH₃ > CH₃ > H > NO₂.

Figure 6. Adsorption of pyrazolone derivatives on metal surfaces in the Metropolis Monte Carlo simulation system of Fe(110)/inhibitors/100H₂O.

Table 8. Adsorption energy of Fe(110)/inhibitor/100H₂O system with Monte Carlo simulation.

Systems	Adsorption energy (inhibitors) kJ·mol ⁻¹	Adsorption energy (water) kJ·mol ⁻¹
Neutral Inhibitor		
Fe(110)/H/100H ₂ O	-122.5352397	-15.76164044
Fe(110)/CH ₃ /100H ₂ O	-141.7897695	-15.78956165
Fe(110)/OCH ₃ /100H ₂ O	-145.5193466	-14.01906377
Fe(110)/NO ₂ /100H ₂ O	-96.90984619	-15.88215498
Protonated Inhibitor		
Fe(110)/H/100H ₂ O	-136.1514453	-15.04476745
Fe(110)/CH ₃ /100H ₂ O	-138.6204407	-15.04068854
Fe(110)/OCH ₃ /100H ₂ O	-141.2104533	-15.48264385
Fe(110)/NO ₂ /100H ₂ O	-129.1357282	-15.77661008

Figure 7. Relationship between adsorption energy and quantum parameters (HOMO, ionization potential, electronegativity, and electron transfer) of neutral inhibitors.

Figure 8. Relationship between adsorption energy and quantum parameters (HOMO, ionization potential, electronegativity, and electron transfer) of protonated inhibitors.

4. Conclusion

The theoretical study of DFT, *ab initio*, and MC simulation were applied to provide a detailed description of pyrazolone derivatives' corrosion inhibition mechanism. The effect of substituents (CH₃, OCH₃, and NO₂) on the efficiency of corrosion inhibition against carbon steel is studied in more detail. Quantum chemical parameters such as frontier molecular orbitals, ionization potential, electronegativity, and electron transfer affect corrosion inhibition efficiency. The quantum chemical parameters show that the electron donor group increases the order OCH₃ > CH₃ > H > NO₂. These results are consistent with experimental studies that have been previously reported by Fouda *et al.* The analysis of the Fukui function shows that the active site of the pyrazolone derivative is at atoms C(1), C(10), N(7), N(8) and O(18). The atom is predominantly involved in the inhibitor interaction with the metal surface. The value of selected stabilization energy (E^2) was obtained as 51.19 kcal/mol from the OCH₃ substituent. It shows that the OCH₃ substituent contributes maximally to corrosion inhibition. The natural bonding orbital analysis results are in line with the results of the MC simulations for inhibitor interaction with the metal surface. This theoretical study is expected to help bridge the gap between experimental studies in

providing a detailed description of the interaction mechanism between inhibitors and metal surfaces.

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