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Adsorption proprieties and inhibition of mild steel corrosion in HCl solution by 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one

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ABSTRACT

*1-Benzyl-4-phenyl-2, 3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** was described as novel potent corrosion inhibitor for mild steel in 1M HCl. The inhibitive characteristic of compound **(P1)** was studied in detail via gravimetric measurement, electrochemical impedance spectroscopy and potentiodynamic polarization. In addition, a quantum chemical study suggests that the 1-Benzyl-4-phenyl-2, 3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** ring involved in this inhibitor is structurally essential for the protection of metal surface.*

Key words: 1, 5-benzodiazepin-2-one, Electrochemical methods, Mild steel, 1M HCl, Polarization, DFT.

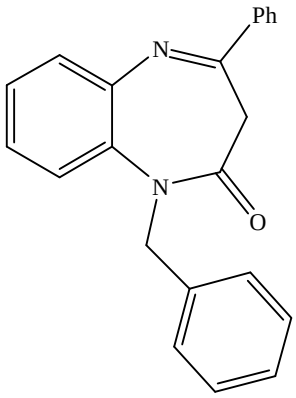
INTRODUCTION

1,5-Benzodiazepines derivatives constitute an important class of psychopharmacopea, in particular as tranquilizer and also as potent virucides and non-nucleoside inhibitors of HIV-1 reverse transcriptase. Beside this, 1, 5-benzodiazepines show antifeedant, anti-inflammatory, analgesic [1], antifungal [2], antianxiety [3], anticonvulsant [4], antispasmodic, antidepressive [5], depressants [6], anxiolytic [7-8], antagonist [9], psychotropic [10], anthelmintic [11], antimicrobial [12] and anticancer activities [13].

The present study aimed to test new compounds named 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** on the corrosion of mild steel in 1 M hydrochloric acid solution. In this work, we are interested in the synthesis of the title compound inhibitors, by alkylation reaction involving with benzyl chloride, and 4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** in DMF (**Scheme 1**).

The use of inhibitors is the most important method for protecting metals from corrosion, and many scientists are conducting research on this topic. New inhibitors are discovered every day. In principle, inhibitors prevent the corrosion of metal by interacting with the metal surface via adsorption through the donor atoms, Π-orbitals, electron density and the electronic structure of the molecule [14-16].

The aim of this study is to evaluate the corrosion inhibition of mild steel in 1M hydrochloric acid with 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** synthesized and showed in **Scheme 1**. Inhibition performance was evaluated by measuring weight loss and electrochemical techniques [17], potentiodynamic polarization measurements [18], electrochemical impedance spectroscopy technique (EIS) [19-20] and quantum chemical study.



Scheme 1: 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)

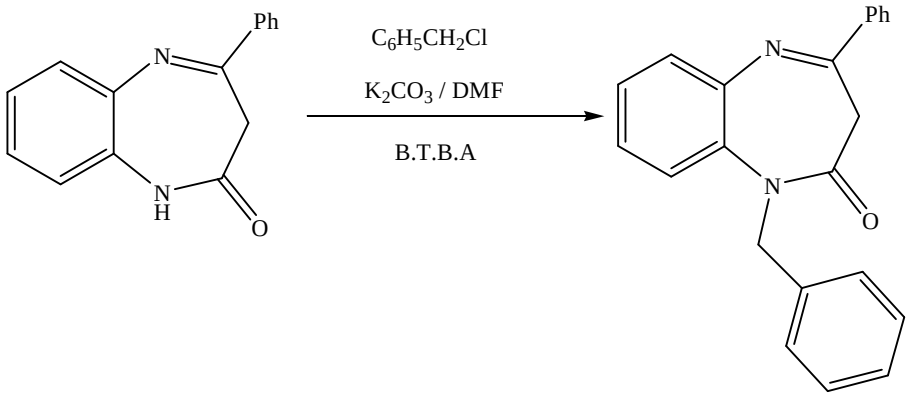
MATERIALS AND METHODS

2.1. Solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water. The concentration range of green inhibitor employed was 10^{-3}-10^{-6}(M).

2.2. Synthesis of inhibitors

To a solution of 4-phenyl-1, 5-benzodiazepin-2-one (1 g, 4.2 mmol) and Benzyl chloride (0.5 ml, 4.2 mmol), in DMF (20 mL), were added 0, 5 mmol of tetra-n-butylammonium bromide and (0,7g, 5mmol) of anhydrous potassium carbonate. After filtration, the solvent was evaporated under reduced pressure and crude residue was recrystallized from ethanol giving the compound 1-benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** in 86% yield **Scheme 2**.



Scheme 2: Synthesis of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)

The analytical and spectroscopic data are conforming to the structure of compound formed.
(P1):**Yield** = 86%; **M.p.**401-402K; **RMN^{1}H (DMSO-d6) δ ppm :** 3.15(d, 1H); 4.22(d,1H); 5.14(s, 2H); 7.07-7.55(m,12H), 8.11-8.17(m, 2H); **RMN^{13}C (DMSO-d6) δ ppm :** 39.98(CH_2); 51.25(NCH_2); 122.21-131.19 (CHar); 108.73(Car); 142.19(Car); 137.21(Car); 135.15(Car); 161.16(C=N);165,9(C=O).

2.3. Experimental techniques

2.3.1. Weight loss measurements

Coupons were cut into 1.5× 1.5 × 0.05 cm^3 dimensions having composition (0.09 % P, 0.01 % Al, 0.38 % Si, 0.05 % Mn, 0.21 % C, 0.05 % S and Fe balance) used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 400, 800, 1000, 1200 grades of emery papers. The specimens are washed thoroughly with bidistilled water degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 100 cm^3. The immersion time for the weight loss is 6 h at (308±1) K. In order to get good reproducibility, experiments were carried out in duplicate. The average weight loss was obtained. The corrosion rate (**v**) is calculated using the following equation:

$$v = W / S.t \quad (1)$$

Where W is the average weight loss, S the total area, and t is immersion time. With the corrosion rate calculated, the inhibition efficiency (Ew) is determined as follows:

$$Ew\ \% = \frac{V0-V}{V0} X\ 100 \quad (2)$$

Where $\mathbf{V_0}$ and **V** are the values of corrosion rate without and with inhibitor, respectively.

2.3.2. Electrochemical tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster software. This potentiostat is connected to a cell with three electrode thermostats with double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. Anodic and cathodic potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from −800 mV to −200 mV at 308 K. The solution test is there after de-aerated by bubbling nitrogen. Inhibition efficiency (Ep %) is defined as Equation3, where icorr(0) and icorr(inh) represent corrosion current density values without and with inhibitor, respectively.

$$Ep\% = \frac{icor(0)-icor(inh)}{icor(0)} x\ 100 \quad (3)$$

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at Ecorr after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 MHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 308 K. The impedance diagrams are given in the Nyquist representation. Inhibition efficiency (E_R%) is estimated using the relation 4, where $R_t(0)$ and Rt(inh) are the charge transfer resistance values in the absence and presence of inhibitor, respectively:

$$ER\% = \frac{Rt(inh)-Rt(0)}{Rt(inh)} x\ 100 \quad (4)$$

2.4. Theoretical calculations

Quantum chemical calculations were performed to investigate the effect of structural electronic parameters on the inhibition efficiency of inhibitor. Geometric and electronic structure of the inhibitor was calculated by the complete geometrical optimization in their neutral form. In order to estimate some of the previous descriptors, the Koopmans' theorem was used [21] to relate the HOMO and LUMO energies to the IP and EA, respectively:

$$IP = -E_{HOMO} \quad (5)$$

$$EA = -E_{LUMO} \quad (6)$$

Then the electronegativity and the global hardness were evaluated, based on the finite difference approximation, as linear combinations of the calculated IP and EA.

$$\chi = \frac{IP + EA}{2} \quad (7)$$

$$\eta = \frac{IP - EA}{2} \quad (8)$$

RESULTS AND DISCUSSION

3.1. Electrochemical measurements

3.1.1. Electrochemical impedance spectroscopy (EIS)

To test preliminarily the inhibitive effect of the title compound 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** for mild steel in 1 M HCl, the electrochemical process of mild steel electrode at the open-circuit potential was first examined via EIS. 1-Benzyl-4-phenyl-2, 3-dihydro-1H-1, 5-benzodiazepin-2-one **(P1)**

were used as the reference compound, and the corresponding Nyquist plots are shown in Figure 1. In the absence of the compound, the capacitive loop of the electrode in HCl, which features a depressed semicircle, was recorded.

The diameter of the capacitive loop increased obviously with gradually increased inhibitor concentrations indicating that the inhibitive effect of 1-Benzyl-4-phenyl-2, 3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** against HCl corrosion is concentration dependent. The electrochemical parameters calculated using the same equivalent circuit model shown in Figure 2 are summarized in Table 1. The C_{dl} values decreased and R_{ct} increased with the increasing concentration of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)**, which indicates a decrease in both the active surface area and corrosion rate caused by the adsorption of the inhibitor.

The decrease in the capacitance was probably caused by the decrease in local dielectric constant and/or an increase in the thickness of double layer due to the replacement of water and some ions originally adsorbed on the metal surface by the inhibitor molecules [23-26].

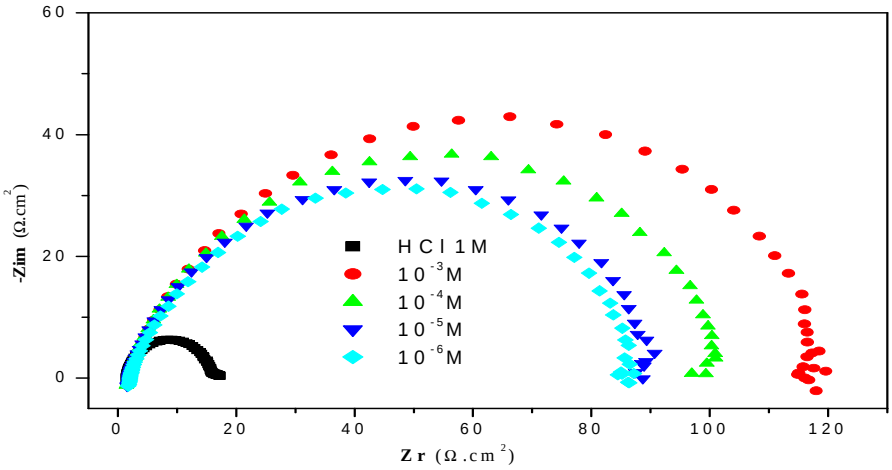


Figure 1. Nyquist plot at different concentrations of 1-Benzyl-4-phenyl-2, 3-dihydro-1H-1,5-benzodiazepin-2-one (P1) in 1M HCl solution

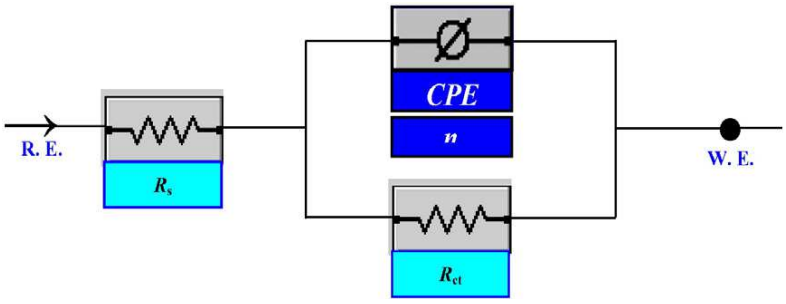


Figure 2. Equivalent circuit used to fit the obtained impedance spectra for mild steel in the presence or absence of various concentration of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)

Table 1. Impedance parameter values for the corrosion of mild steel in 1M HCl

Inhibitor	Concentration (M)	R_t ($\Omega.cm^2$)	C_{dl} ($\mu F.cm^{-2}$)	E_{Rt} (%)
1M HCl	-	14.50	200	-
1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)**	10^{-6}	87	85	79
	10^{-5}	92	73	82
	10^{-4}	102	63	85
	10^{-3}	121	35	89

3.1.2. Potentiodynamic polarization measurements

Polarization curves for the mild steel in 1 M HCl in the absence and presence of different concentrations of 1-Benzyl-4-phenyl-2, 3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** are shown in Figure 3. The corresponding electrochemical parameters including corrosion potential (E_{corr}), Tafel slope (βc), corrosion current density (I_{corr}) and inhibition efficiency (E_p) are given in Table 2. Clearly, upon increase of the inhibitor, both βc values varied accordingly and the I_{corr} values decreased prominently.

This means that both anodic metal dissolution of mild steel and cathodic hydrogen evolution reaction were inhibited. Moreover, the g values obtained from Tafel extrapolation are in good agreement with those obtained from EIS and gravimetric methods. The corrosion potential of mild steel shifted 5–18 mV with respect to that of the blank, which suggests that 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** behaves as a mixed type corrosion inhibitor for mild steel[27-30] by first adsorbing on the metal surface and then blocking the reaction sites of the metal surface without affecting the anodic and cathodic reaction [31].

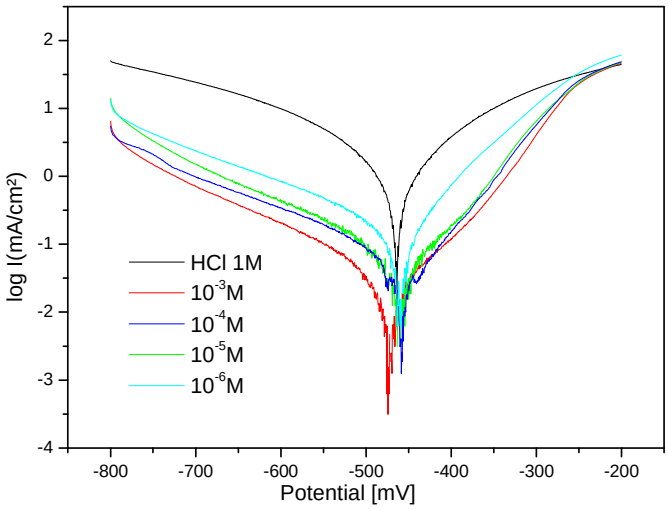


Figure 3: Tafel plot of mild steel with different concentrations of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1) in 1M HCl solution

Table 2: Tafel polarization parameters obtained at different concentrations of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)

Inhibitor	Concentration (M)	$-E_{corr}$ (mV/SCE)	Icorr ($\mu A/cm^2$)	-βc	E_p (%)
1M HCl	-	465	1386	164	--
1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)**	10^{-6}	483	483	167	65
	10^{-5}	460	318	151	77
	10^{-4}	462	217	140	84
	10^{-3}	475	136	139	90

3.2. Gravimetric measurement

Gravimetric measurement which is a reliable and concise analytical method was also used for the study of the inhibitive effect of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** under different concentrations [32-33]. To ensure the reproducibility, experiments were performed for three times and the average results are compiled in Table 3 and figure 4. Clearly, with gradually increased inhibitor concentrations the weight loss as well as the corrosion rate (*w*) of the mild steel diminished distinctly, which is in agreement with the results obtained by EIS and polarization. An excellent inhibitory efficiency (E_w) assigning to 91% was acquired at the highest inhibitor concentration applied (10^{-3} M).

Table 3. Corrosion parameters obtained from weight loss measurements for mild steel in 1 M HCl containing various concentrations of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1) at 308 K

Inhibitor	Concentration (M)	Wcorr ($mg.cm^{-2}.h^{-1}$)	Ew (%)	θ
HCl 1M	--	0.82	--	--
1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)**	10^{-6}	0.33	60	0.60
	10^{-5}	0.17	79	0.79
	10^{-4}	0.09	89	0.89
	10^{-3}	0.07	91	0.91

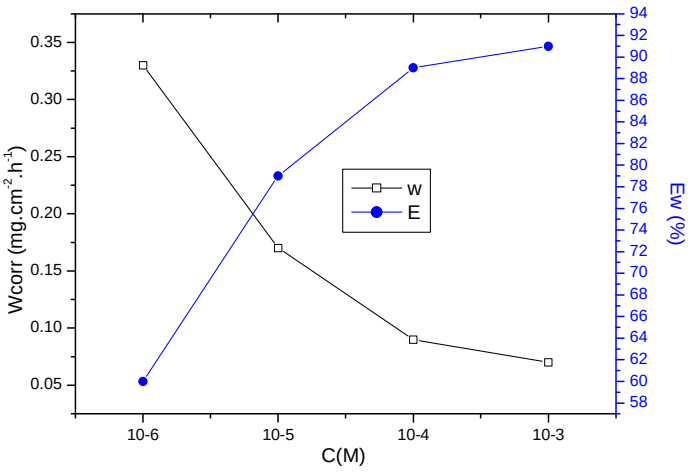


Figure 4. The corrosion rate and the inhibition efficiency E_w% for Mild steel in 1 M HCl containing different concentrations of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)

3.3. Adsorption Isotherm

Adsorption isotherm experiments were subsequently conducted to evaluate the adsorption process of P1 for gaining more insight into its inhibitive mechanism. The surface coverage values (θ) with an inhibitor concentration of 10^{-3} M were examined by tentatively fitting to Temkin, Frumkin, Freundluich and Langmuir isotherm models, respectively [34-35]. As a result, the best correlation between the experimental results and isotherm functions was obtained using Langmuir adsorption isotherm:

$$\frac{C}{\theta} = \frac{1}{k} + C \qquad \textbf{(9)}$$

Where, C is the concentration of inhibitor, θ is surface coverage on the metal surface and K_{ads} is the equilibrium constant of adsorption process. The correlation coefficient (R^2= 0.989) was used to choose the isotherm that best fit experimental data.

Plotting of C vs. C/θ results in a linear correlation, shown in Figure 5. The standard free energy of adsorption, $\Delta G°_{ads}$ is related to the K_{ads} with the equation given below:

$$K = \frac{1}{55.55}\exp(-\frac{\Delta G^{0}_{ads}}{RT}) \qquad \textbf{(10)}$$

Where 55.5 is the molar concentration of water in the solution expressed in molarity units (M) [36].

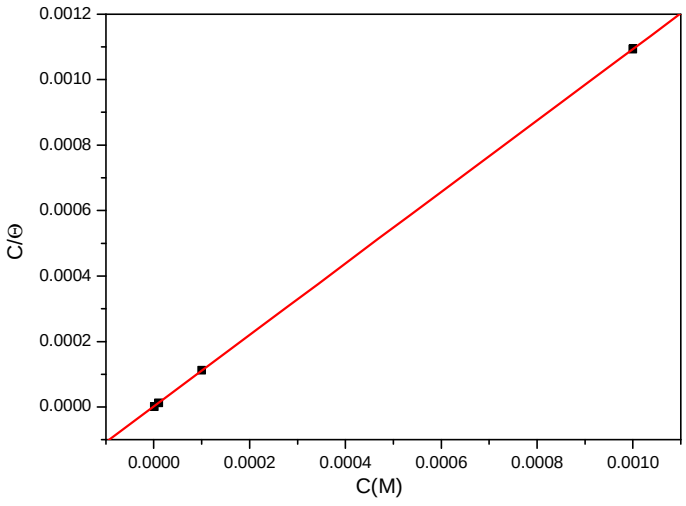


Figure 5. Langmuir isotherm plots for the adsorption of inhibitor on mild steel

As shown in Table 4, the negative $\Delta G°_{ads}$ value (- 44.18) obtained indicates that the adsorption process of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** to the surface is spontaneous and the interaction of the adsorbed layer with the steel surface is stable [37]. Meanwhile, it could be deduced that inhibitor 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** adopts both electrostatic-adsorption and chemisorptions on the mild steel surface in 1 M HCl with the latter being privileged [38-39].

Table 4. The calculated value of K_{ads} and $\Delta G°_{ads}$ for mild steel in 1 M HCl containing compound 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1) at 308

Inhibitor	Slope	R^2	K_{ads} (M^{-1})	$\Delta G°_{ads}$ (kJ mol^{-1})
1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)**	1.0917	0.989	5.66 10^5	- 44.18

3.4. Quantum chemical calculations

Quantum chemical calculations are used to correlate experimental data for inhibitors obtained from different techniques (viz., electrochemical and weight loss).

The obtained molecular structure HOMO and LUMO orbitals of the neutral inhibitor molecule by DFT/B3LYP/6-31G(d, p) [40-42] obtained from the DFT calculations are given in **Figure 6**.

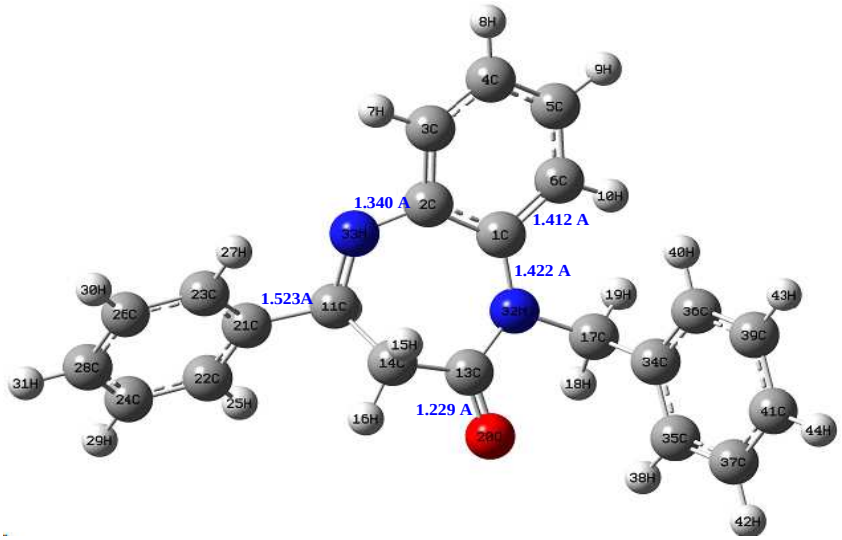


Figure 6. Optimized structures and bond lengths of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)

After the analysis of the theoretical results obtained, we can say that the molecule have a non-planar structure.

The smaller gap (ΔE) between E_{HOMO} and E_{LUMO} is the more probable to donate and accept electrons. The values of ΔE in Table 5, suggesting the strongest ability of the synthesized inhibitor to form coordinate bonds with d-orbitals of metal through donating and accepting electrons, is in good agreement with the experimental results. Additionally, for the dipole moment (μ), higher value of μ will favor the enhancement of corrosion inhibition [43-44]. From Table 5, the value of μ is higher, which is also in agreement with the experimental results mentioned above.

Table 5. Calculated quantum chemical parameters of the compound 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)

Quantum Parameters	Inhibitor (P1)
Total energy (eV)	28148.7
E_{HOMO} (eV)	-5.2967
E_{LUMO} (eV)	-0.5951
ΔEgap (eV)	5.089
μ (debye)	2.2160
IE (eV)	5.2967
EA (eV)	0.5951
χ (eV)	2.9459
η (eV)	2.3508

The optimized geometries of the studied compounds in the neutral form including their HOMO and LUMO distributions density are shown in Figure 7.

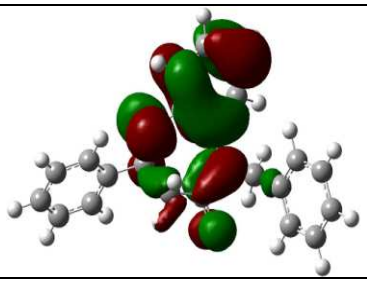
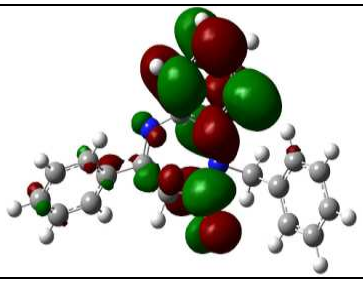
Inhibitor	HOMO	LUMO
1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)**		

Figure 7. The frontier molecular orbital density distribution of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)

CONCLUSION

All performed measurements showed that the P1 as a good inhibitor of the corrosion of mild steel in a 1M HCl solution, the inhibition efficiency increases with increasing concentration of the 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** to the temperature 308K. The inhibitor follows the Langmuir isotherm adsorption, it is due to the adsorption of 1-Benzyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** molecules on the metal surface by charge transfer on the surface of the metal. The correlations between inhibition efficiency and molecular parameters can be used for preselection of new inhibitors. Understanding the phenomena of adsorption is key point in corrosion problems. Computational studies help to find the most probable adsorption sites for a molecule. This information can help to gain further insight into corrosion system, such as the most probable site for inhibitor adsorption.

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