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1-Ethyl-4-phenyl-2,3-dihydro-*1H*-1,5-benzodiazepin-2-one as a new corrosion inhibitor for mild steel in hydrochloric acid

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ABSTRACT

Adsorption of 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one ***(P1)*** *on mild steel surface in 1 M HCl solution and its corrosion inhibition properties has been studied by a series of techniques, such as polarization, electrochemical impedance spectroscopy (EIS), weight loss and quantum chemical calculation methods. Potentiodynamic polarization measurements showed that 1,5-benzodiazepine derivative inhibitor is mixed type. The degree of surface coverage was determined by using weight loss measurements and it was found that adsorption process of studied inhibitor on mild steel surface obey Langmuir adsorption isotherm.*

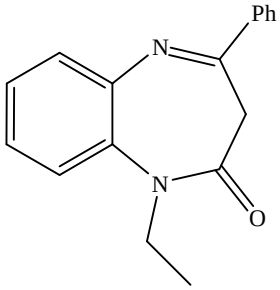
Key words: 4-phenyl-1,5-benzodiazepin-2-one, Mild steel, weight loss, inhibition, Polarization, EIS, Acid corrosion, DFT.

INTRODUCTION

Over the years, Benzodiazepines are an important class of nitrogen containing heterocyclic compounds acting mainly on the central nervous system. They have attracted much attention in the field of medicine and pharmaceuticals due to their broad spectrum of biological activities.

1, 5-Benzodiazepine derivatives have attracted the attention of researchers owing to their interesting pharmacological activities and their low toxicity. They are widely used as anti-anxiety [1], analgesic [2], anti-inflammatory [3], DNA binding activity [4-7], anti-cancer [8-10], anti-tumor [11-12], adenosine binding activity [13], antisialogogic [14], cutaneous anaphylaxis [15], antimicrobial [16-17],anthelmintic, antibacterial, antifungal, diuretic, anthelmintic, antipyretic [18-19], anti-neuroinflammatory [20], antiparkinson [21], antileishmanial [22], muscle relexant [23], anxiolytic [24] , anticonvulsant [25], anti-HIV [26],sedative and hypnotic [27].

The present study aimed to test new compound named 1-Ethyl-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, by realizing the alkylation reaction with ethyl bromide (**Scheme 1**).



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

The present work is aimed to study the corrosion inhibition efficiencies of the newly synthesized 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** on mild steel in 1M HCl using mass loss and electrochemical techniques [28-29].The experimental findings were discussed with quantum chemical calculation methods.

MATERIALS AND METHODS

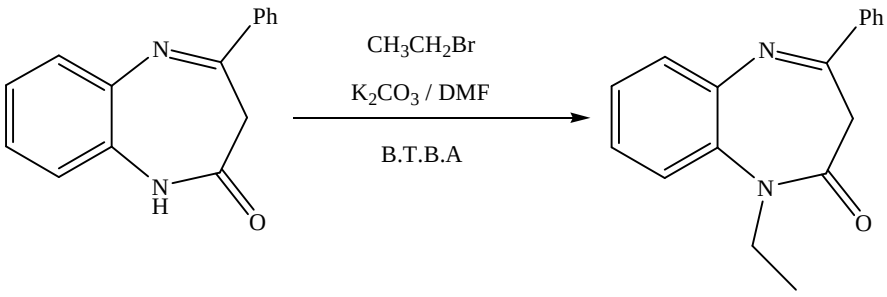
2.1. Materials and sample preparation

The composition (wt.%) of mild steel samples used for all the experiments was as follows: C = 0.253; Si = 0.12; P = 0.013; S = 0.024; Cr = 0.012; Mn = 0.03 and balance Fe. Coupons cut into 1.5 x 1.5 x 0.05 cm size were used for gravimetric measurements whereas specimens of size with 1 cm^2 exposed surface areas were used as working electrode for polarization and EIS measurements. Before starting the experiments, the specimens were mechanically abraded with 320, 400, 600, 800, 1000 and 1200 grade of emery papers. These were then degreased with acetone, washed with double distilled water and dried in air before immersing in the corrosive medium.

The corrosive solution, 1.0 M HCl was prepared by dilution of analytical grade HCl of predetermined normality with triple distilled water. The concentration range of 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** used was 10^{-6} M to 10^{-3} M. The volume of electrolyte used in each experiment was 100 ml.

2.2. Synthesis of inhibitors

To a solution of 4-phenyl-1,5-benzodiazepin-2-one (1 g, 4.2 mmol) in DMF (20 ml) was added ethyl bromide (0.46 g, 4.2 mmol), potassium carbonate (1 g, 7.4 mmol) and a catalytic quantity of tetra-n-butylammonium bromide. The mixture was stirred at room temperature for 24 h. The solution was filtered and the solvent removed under reduced pressure. The residue was recrystallized from ethanol to afford the compound as yellow crystals in 70% yield (**Scheme 2)**.



Scheme 2: Synthesis of 1-Ethyl-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 =** 70%; **M.p.**363-365**K**; **RMN^{1}H (DMSO-d6) δ ppm:** 1.2 (t, 3H) ; 2.95 (d, 1H) ; 3.9 (q, 2H) ; 4.05 (d, 1H) ; 7.00-7.9 (m, 9H).; **RMN^{13}C (DMSO-d6) δ ppm:** 13.11 (CH_3); 35.85 (CH_2); 42.2 (NCH_2); 111.47- 129.64 (CHar); 127.17 (Car); 139.12 (Car); 141.49 (Car); 143.16 (C=N); 172,93 (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 bid stilled 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:

$$\mathbf{v = W / S.t} \quad \textbf{(1)}$$

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:

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

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 polarization 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.

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

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:

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

2.4. Quantum chemical 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 [30] to relate the HOMO and LUMO energies to the IP and EA, respectively:

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

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

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

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

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

RESULTS AND DISCUSSION

3.1. Weight loss measurements

Corrosion of mild steel in 1 M HCl containing different concentrations of 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** was studied by weight loss measurements, that is, measuring the mass of metal turned into corrosion products per unit area of surface per unit of time.

The corrosion rate (ρ) in mg cm^{-2} h^{-1} in the absence and presence of 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** was determined using the following equation:

$$\rho = \frac{\Delta W}{At} \quad \textbf{(9)}$$

Where ΔW is the average weight loss of the mild steel specimens, A is the total area of mild steel specimen and t is the immersion time. The percentage inhibition efficiency (E %) was calculated using the relationship:

$$E\ (\%) = \frac{W0 - Wi}{W0} \times 100 \quad \textbf{(10)}$$

Where and Wi are the weight loss values in the absence and presence of 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)**. At this point, it is worth mentioning that all data presented below in Figures and Tables related to corrosion rate and inhibition efficiency, were calculated from weight loss measurements.

Table 1.weight loss mesurements of different concentration with and without presence of 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)

Inhibitor	Concentration (M)	Corrosion rate (mg/cm².h)	Efficiences %
1M HCl	-	0.8200	-
Inhibitor (P1)	$\mathbf{10^{-6}}$	0.45	45
	$\mathbf{10^{-5}}$	0.27	67
	$\mathbf{10^{-4}}$	0.19	77
	$\mathbf{10^{-3}}$	0.08	90

It is clear that with the rise in 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** concentration, corrosion rate decreased and then the inhibition efficiency increased. The highest inhibiting efficiency attained 90% at 10^{-3}M.

3.2. Adsorption Isotherm

The adsorption of inhibitor molecules from aqueous solution is a quasi-substitution process [31-32]. The surface protection of mild steel depends upon how the inhibitor molecule will be adsorbed on the metal surface [32]. The degree of surface coverage (θ) as function of concentration (C) of the inhibitor was studied graphically by fitting it to various adsorption isotherms to find the best adsorption isotherm. Langmuir adsorption isotherm was found to be the best description for 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** on mild steel in 1 M HCl medium. According to this adsorption isotherm, θ is related to the inhibitor concentration, C, and adsorption equilibrium constant, K_{ads}, through the following expression:

$$\frac{C}{\theta} = \frac{1}{k} + C \quad \textbf{(11)}$$

The plot of C/θ versus C gave straight lines (Figure 1) with regression close to unity confirming that the adsorption of 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** on mild steel surface in 1M HCl medium obeys the Langmuir adsorption isotherm. The free energy of adsorption was calculated using the following relations:

$$K = \frac{1}{5555}\exp\left(\frac{\Delta G^0_{ads}}{RT}\right)$$

Where R is the universal gas constant, T is the absolute temperature, K_{ads} is the equilibrium constant for adsorption process, and 55.5 is the molar concentration of water in solution (mol L^{-1}).

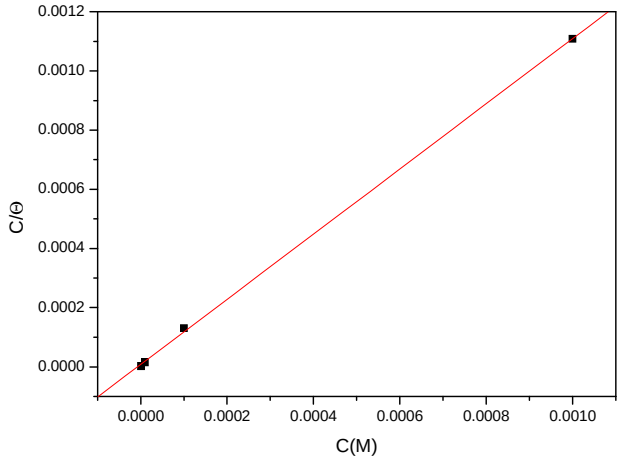


Figure 4. Langmuir isotherm plots for the adsorption of inhibitor on mild steel

Table 2. The calculated value of K_{ads} and $\Delta G°_{ads}$ for mild steel in 1 M HCl containing compound 1-Ethyl-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})
P1	1.10131	0.999	1.26 10^5	-40.33

The calculated parameters are reported in the Table 2. Negative values of the Δ*G*°ads reflect spontaneous adsorption and strong interaction of inhibitory molecules on the surface of the mild steel. In general, values of around or below Δ*G*°ads -20 kJ.mol^{-1} are compatible with physisorption and those around or more negative than -40 kJ.mol-1 involve chemisorptions [33].

3.3. Electrochemical impedance spectroscopy

In order to confirm the results extracted from weight loss and to acquire more information about corrosion mechanisms, EIS measurements were carried out at corrosion potential. The obtained results after immersion in 1 M HCl with and without 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** is presented in Figure 1.

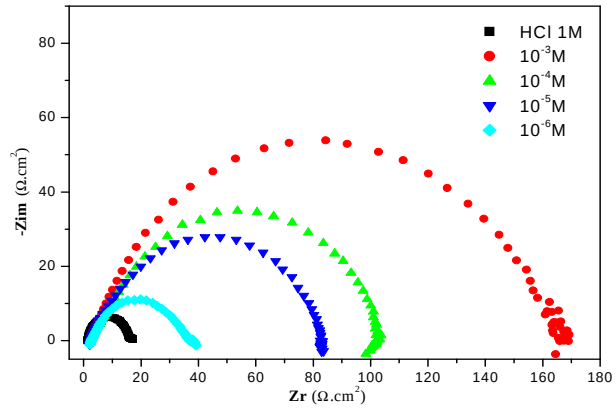


Figure 1. Nyquist plots of mild steel in 1M HCl in presence of different concentrations of inhibitors 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)

Table 3. Impedance parameter values for the corrosion of mild steel in 1M HCl

Inhibitor	Concentration (M)	R_t ($\Omega.cm^2$)	C ($\mu f/cm^2$)	E (%)
1M HCl	-	14.57	200	--
Inhibitor (P1)	**10^{-6}**	36	115	61
	10^{-5}	83	25	82
	10^{-4}	105	20	86
	10^{-3}	166	19	91

For Nyquist plots (Figure 1) it is clear that the impedance diagrams in most cases does not show perfect semicircle. This behavior can be attributed to the frequency dispersion [34-36]. As a result of roughness and in homogenates of the electrode surface. The impedance response consisted of characteristic semicircles for solutions examined indicating that the dissolutions of mild steel process occurs under charge transfer control in other words under activation control and the presence of the inhibitor does not change the mechanism of the acid dissolution. These semicircles are of a capacitive type whose diameters increase with increasing inhibitor concentration. The data indicate that increasing charge transfer resistance is associated with a decrease in the double layer capacitance and increase in the percentage inhibition efficiency.

3.4. Potentiodynamic polarization measurements

Anodic and cathodic polarization curves for mild steel in 1M HCl with and without various concentrations of used inhibitor 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** are shown in figure 2.

The values of electrochemical parameters associated with polarization measurements, such as corrosion potential (E_{corr}), corrosion currents densities (I_{corr}) and cathodic Tafel slope (βc) are listed in Table 3.

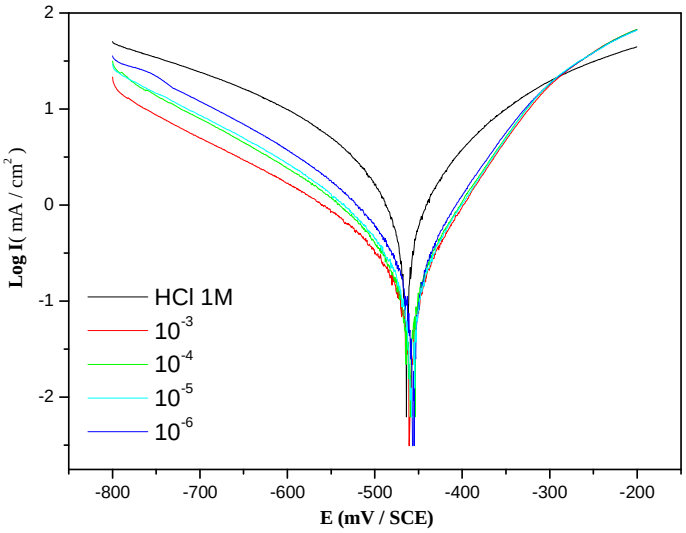


Figure 2. Tafel plot of mild steel with different concentrations of 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1) in 1 M HCl solution

It is clear from the Figure 2, that both anodic metal dissolution and cathodic hydrogen reduction reactions were inhibited when the 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** inhibitor was added to 1M HCl. The corrosion potential is almost unchanged. The corrosion current density as well as corrosion rate of mild steel considerably reduced in the presence of the inhibitor.

Table 3. Polarization parameters and corresponding inhibition efficiency for the corrosion of the mild steel in 1M HCl without and with addition of various concentrations of 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1) at 308k

Inhibitor	Concentration (M)	$-E_{corr}$ (mV/ECS)	I_{corr} (μA/cm^2)	$-\beta_c$ (mV/dec)	E (%)
1M HCl	-	455	1205	187	--
Inhibitor (P1)	**10^{-6}**	457	451	138	63
	10^{-5}	459	269	148	78
	10^{-4}	453	205	155	83
	10^{-3}	450	101	152	92

The results are indicative of the adsorption of inhibitor molecules on the mild steel surface. The inhibition of both anodic and cathodic reactions is more marked with the increasing inhibitor concentration while the corrosion potential nearly remained the same in comparison with corrosion potential observed in blank solution.

These results indicate that the 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** is a mixed-type inhibitor for the corrosion of mild steel in 1M HCl [37-38].

3.5. Molecular geometries

The use of quantum chemical calculations is very important in establishing the correlation between molecular structure and corrosion inhibition efficiency. The effectiveness of an inhibitor is related to its spatial and electronic molecular structures [39]. The obtained molecular structure and HOMO and LUMO orbitals of the neutral inhibitor molecule by DFT/B3LYP/6-31G(d, p) [40-41] obtained from the DFT calculations are given in **Figure 3**.

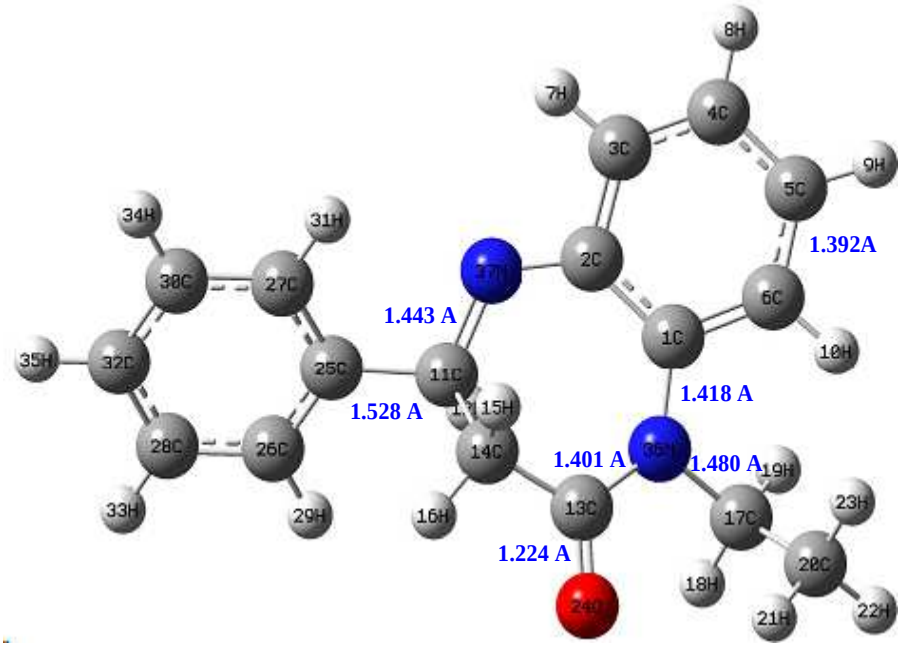


Figure 3. Optimized structures of 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)

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 4, 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 [42-43]. From Table 4, the value of μ is higher, which is also in agreement with the experimental results mentioned above.

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

Quantum Parameters	Inhibitor (P1)
Total energy (eV)	22931.8
E_{HOMO} (eV)	-5.8607
E_{LUMO} (eV)	-1.8087
ΔEgap (eV)	5.089
μ (debye)	2.9428
IE (eV)	5.8607
EA (eV)	1.8087
χ (eV)	3.8347
η (eV)	2.0260

The optimized geometries of the studied compounds in the neutral form including their HOMO and LUMO distributions density are shown in Figure 4.

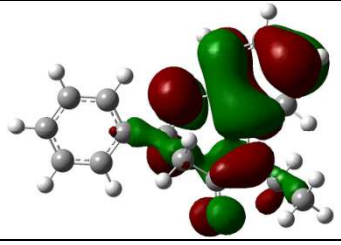
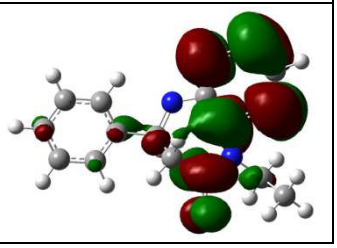
Inhibitor	HOMO	LUMO
1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (P1)		

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

CONCLUSION

The synthesized inhibitor 1-Ethyl-4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one **(P1)** characterized by ^{1}H-NMR, and mass spectral studies. It was found that the effective corrosion inhibitor. The results obtained from the mass loss measurements were in good agreement with those obtained from the potentiodynamic polarization and EIS methods. The process obeyed the Langmuir adsorption isotherm. The selection of parameters is in important step in theoretical study. The relationship between the parameter(s) and activity should be strong, and therefore efficiency predictions will be more promising. Structural and electronic parameters from the quantum chemical calculations are correlated well to the experimentally obtained inhibition efficiencies.

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