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Inhibition Study of Mild Steel Corrosion in Hydrochloric Acid by 1, 5-Benzodiazepine-2,4-dione

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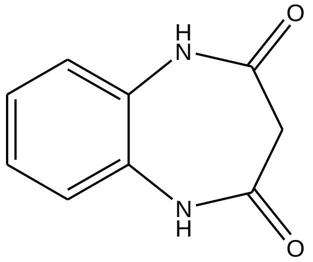
Abstract

The inhibition of corrosion of mild steel in a molar hydrochloric acid solution of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1) was studied at 308 K using electrochemical and chemical methods. The results showed that compound was good inhibitor and the inhibition efficiency increases with the concentration of inhibitor studied rise. An explanation by the calculations of quantum chemistry to be correlated with an efficiency of inhibition of the test compound is discussed using the method of the density functional theory (DFT).

Keywords: Mild steel, 1,5-Benzodiazepine-2,4-dione, Corrosion inhibition, Hydrochloric acid.

1. Introduction

The synthesis of heterocyclic benzodiazepine derivatives aroused the enthusiasm of researchers. Benzodiazepines are effective in minimizing anxiety and stress, and have fewer and less severe[1-2].Studies have shown that such compounds are widely involved in several fields such as pharmacology [3], anticancer [4] and anxiolytic agent [5]. The different compounds of benzodiazepines present most of the properties of corrosion inhibitors [6]. Effective inhibitors are organic compounds which primarily contains the hetero atoms such as sulfur, phosphorus, nitrogen and oxygen[7-8]; although an organic molecule has become a concern health and the environment[9-10]. The aim of the present study is to evaluate the corrosion inhibition efficiency of mild steel in 1 M hydrochloric acid solution by: 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione, **Scheme 1** shows the molecular structure of the organic compound that have been studied, produced by the condensation *o*-phylenediamine with malonic acid in HCl (4N) The structure of the product obtained is determined by spectroscopic and elemental analysis.

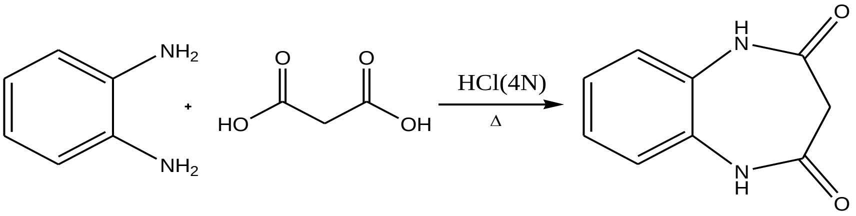


Sheme 1: Chemical structure of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione.

2. Experimental details

2.1. Synthesis of inhibitors

The 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione was synthesized by the condensation of 18.5mmol *o*-phenylenediamine with 18.2 mmol of malonic acid under moderate heat for 6 hours in 20 ml hydrochloric acid solution (4N).



Sheme 2: Synthesis of1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione

Melting points were measured on a kofler.NMR spectra were recorded in DMSO-d_6 are conforming the chemical structure proposed.

(P1):Yield = 95%; **M.p**>533 K; **^{1}H NMR (DMSO- d_6) δ ppm :** 3.62 (s, 2H, CH_2-C=O) ; 10.41(s,1H,NH) ;10.45(s,1H,NH);7.03-7.30 (m,4H,CH-ar). **^{13} C NMR(DMSO- d_6) δ ppm :** 164.78-164.67 (2 C=O); 136.14; 134.13 ; 131.05 (Cq); 127.20 125.29 ; 123.42 (CH-ar); 44.42 (CH_2-CO).

2.2. 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 P1 inhibitor employed was 10^{-6} -10^{-3} (M).

2.3. 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:

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

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:

$$\mathrm{Ew}\,\% = \frac{V0-V}{V0}\ \mathrm{X}\ 100 \qquad \mathbf{(2)}$$

Where V_o and $V$are the values of corrosion rate without and with inhibitor, respectively.

2.4. Electrochemical measurements

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster soft-ware. 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 $i_{corr(0)}$ and $i_{corr(inh)}$ represent corrosion current density values without and with inhibitor, respectively.

$$Ep\% = \frac{\mathrm{icor\ (0)} - \mathrm{icor\ (inh\,)}}{\mathrm{icor\ (0)}}\mathrm{x}\ 100 \qquad \mathbf{(3)}$$

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:

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

2.5. Quantum chemical calculations

The quantum chemical calculations, of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1), reported in this work are performed at the B3LYP/6-31G (d,p) level of theory using GAUSSIAN 09 series of programs[11]. The optimizations of equilibrium geometrie of the 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1)derivative were performed using the Berny analytical gradient optimization method [12, 13]. The electronic populations as well as the Fukui indices and local nucleophilicities are computed using different populations analysis MPA (Mulliken population analysis) and NPA (natural population analysis) [14-17]. The cationic systems, needed in the calculation of nucleophilic Fukui indices, are taken in the same geometry as the neutral system.

The aim of this study is to investigate computationally inhibitory action of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1)with chloridric acid in gas and in aqueous phase using B3LYP methods with 6-31+G(d,p) basis set.

3. Results and discussion

3.1. Electrochemical measurements

3.1.1. Potentiodynamic polarization studie

Figure 1shows the typical potentiodynamic polarization curves of mild steel in 1 M HCl solution in the presence and absence of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1)at different concentration.

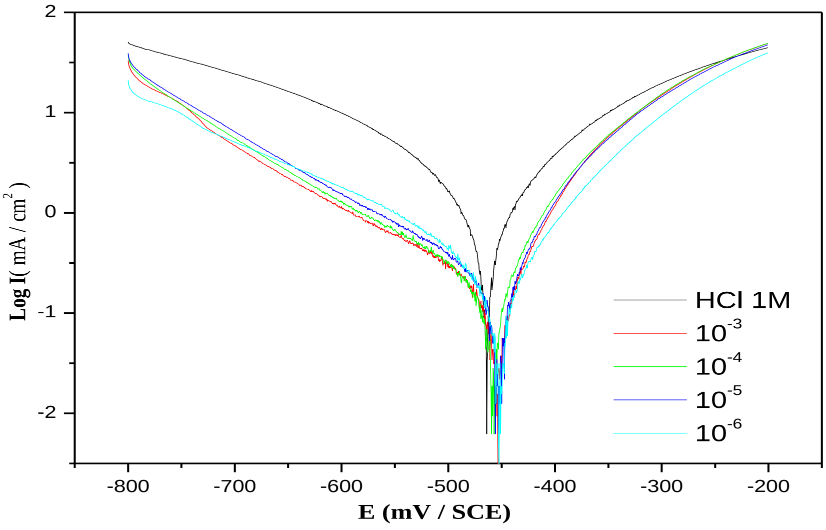


Figure 1. Tafel plot of mild steel with different concentrations of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1) in 1M HCl solution

As can be seen from the figure after addition of inhibitor a decrease in both cathodic and anodic currents was observed, suggesting that the presence of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1)reduced anodic dissolution and also retarded the hydrogen evolution reaction [18]. Table 1 shows the electrochemical corrosion kinetic parameters, i.e. corrosion potential (Ecorr), cathodic Tafel slopes (βc) and corrosion current density (Icorr) obtained from the Tafel extrapolation of the polarization curves. Table 1 also included percentage inhibition efficiency (E%).

These results show that the inhibition efficiency increased, while the corrosion current density decreased with the addition of inhibitors. This may be due to the adsorption of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1)on mild steel/acid interface.

It is clear from Table 1 that there is a small shift towards cathodic region in the values of corrosion potential (Ecorr). In literature, it has been reported that [19] if the displacement in Ecorr (i) is >85 mV with respect to Ecorr, the inhibitor can be seen as a cathodic or anodic type and (ii) if displacement in Ecorr is <85, the inhibitor can be seen as mixed type. In our study the maximum displacement in Ecorr value was 14 mV towards cathodic region, which indicates that all studied 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1) is mixed type inhibitor [20].

Table 1. Polarization parameters and corresponding inhibition efficiency for the corrosion of the mild steel in 1M HCl without and with addition of various concentrations of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1)at 308K.

Inhibitor	**Concentration** (M)	**-E$_{corr}$** (mV/ECS)	**I$_{corr}$** (μA/cm^2)	**-β$_c$** (mV/dec)	**Ep** (%)
1M HCl	--	465	1205	187	--
Inhibitor **(P1)**	**10^{-6}**	451	700	179	42
	10^{-5}	453	513	173	57
	10^{-4}	460	302	174	75
	10^{-3}	455	101	177	92

3.1.2. Electrochemical impedance measurements

The impedance measurements were carried out after immersion for 30 min in 1 M HCl solutions in absence and presence of different concentration of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1). Figure 2 shows typical Nyquist plots for mild steel in 1 M HCl in the absence and presence of studied inhibitor at 308 K. The Nyquist plots show a depressed capacitive loop in the high frequency (HF) range. The HF capacitive loop can be attributed to the charge transfer reaction and time constant of the electric double layer and to the surface in homogeneity of structural or interfacial origin, such as those found in adsorption processes [21].

It is obvious that addition of inhibitor resulted in an increase in diameter of the semicircular capacitive loop (Figure 2) and in the impedance of the double layer (Figure 3) impedance.

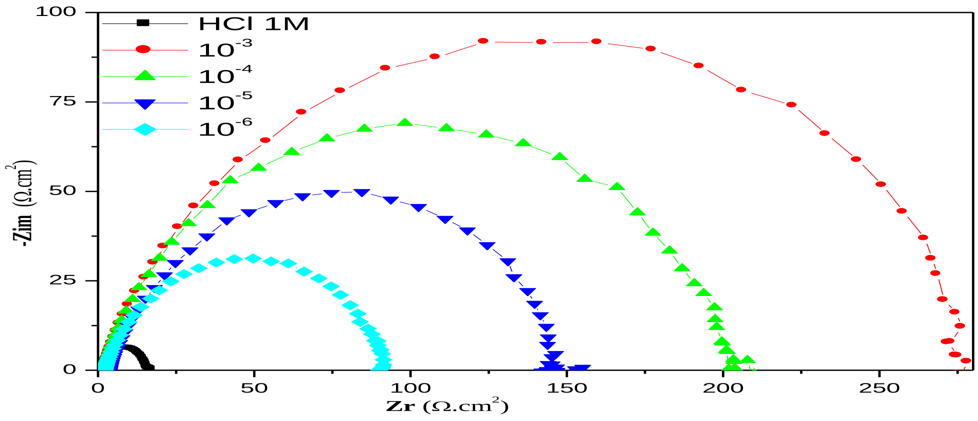


Figure 2. Nyquist plots of mild steel in 1M HCl in presence of different concentrations of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1).

Based on the shape of Nyquist plots (Figure 3) we decided to use the simplest equivalent circuit for a system in which the Warburg impedance is unimportant to fit the impedance measurements. This equivalent circuit (Figure 3) includes the solution resistance (Rs), the charge-transfer resistance (Rt) whose value is a measure of electron transfer across the surface and is inversely proportional to corrosion rate and a constant phase element (CPE), instead of the double layer capacitor (C_{dl}), in order to take into account the electrode surface heterogeneity resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, formation of porous layers [22, 23].

Table 2. Impedance parameter values for the corrosion of mild steel in 1M HCl.

Inhibitor	**Concentration**(M)	R_{ct}(Ω.cm^2)	C_{dl}(μf/cm^2)	**E**(%)
1M HCl	--	15	200	--
Inhibitor (P1)	10^{-3}	274	36	93
	10^{-4}	198	49	90
	10^{-5}	133	65	87
	10^{-6}	83	90	80

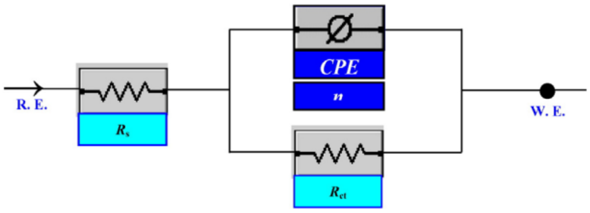


Figure 3. Equivalent circuit used to fit the obtained impedance spectra for mild steel in the presence or absence of various concentration of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1).

3.2. Weight loss measurements

3.2.1. Effect of inhibitor concentration

Corroborative results between weight loss and other techniques have been reported [21-24]. The corrosion parameters obtained by conducting weight loss measurements for mild steel in the absence and presence of different concentration of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1)in 1 M HCl are listed in Table 3.

Table 3. Corrosion parameters obtained from weight loss measurements for mild steel in 1 M HCl containing various concentrations of P1 at 308 K.

Inhibitor	**Concentration** (M)	**Wcorr** (mg.cm^{-2}.h^{-1})	**Ew** (%)	**θ**
HCl 1M	--	0.82	--	--
Inhibitor (P1)	10^{-6}	0.25	70	0.70
	10^{-5}	0.17	79	0.79
	10^{-4}	0.13	84	0.84
	10^{-3}	0.07	91	0.91

The data in Table 3 show that the corrosion rate values decrease as the concentrations of the inhibitor increase, i.e. the corrosion inhibition efficiency increases upon increasing the inhibitor concentration. This behavior is due to the adsorption and the coverage of inhibitor on iron surface [24].

3.2.2. Adsorption Isotherm

Organic inhibitors were found to protect iron and mild steel from corrosion in acid medium by their adsorption on metal surface. In order to gain more information about mode of adsorption of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1)on iron surface in 1 M HCl at temperature studied, attempts were made to fit experimental data with several adsorption isotherms like Temkin, Langmuir, Freundlich, Frumkin, Bockris–Swinkels and Flory–Huggins isotherms. The best fit was obtained with Langmuir's isotherm, which is in good agreement with Eq. (5).

$$\frac{C}{\theta} = \frac{1}{k} + C \quad \textbf{(5)}$$

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.

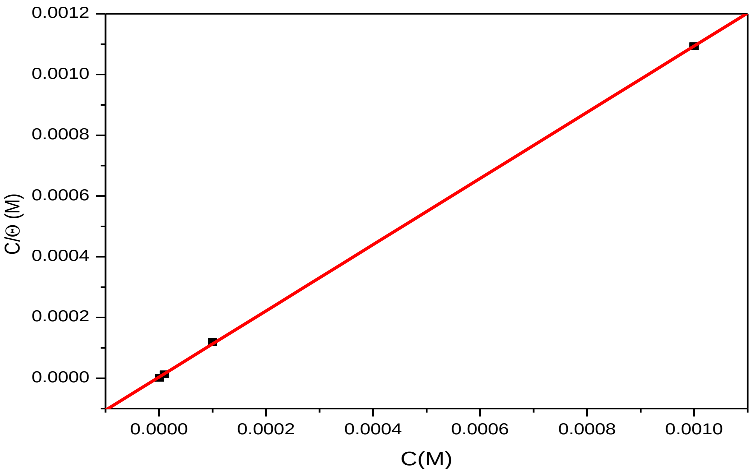


Figure 4. Langmuir's isotherm adsorption model of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1) on the mild steel surface in 1 M HCl at 308K.

The plots of C_{inh}/θ against C_{inh} were straight lines with almost unit slopes and are shown in Figure 4. It is found that all the regression coefficients are very close to 1 which indicates that the adsorption of TMPA on the mild steel surface obeys Langmuir adsorption isotherm. The free energy of adsorption $\Delta G°_{ads}$, also can be calculated using the following equation:

$$K = \frac{1}{55.55} exp\left(\frac{\Delta G^0_{ads}}{RT}\right) \textbf{(6)}$$

Where *R* is the universal gas constant, T the thermodynamic temperature and the value 55.5 is the molar concentration of water in the solution.

ΔG°ads indicate the stability of the adsorbed layer on the mild steel surface and spontaneity of the adsorption process. It is well known that values of ΔG°ads around −20 $kJ.mol^{-1}$ or lower are associated with the physisorption phenomenon where the electrostatic interaction assemble both the charged molecule and the charged metal, while those around −40 $kJ.mol^{-1}$ or higher are associated with the chemisorption phenomenon where the sharing or transfer of organic molecules charge to the metal surface takes place [25, 26]. The calculated ΔG°ads value was found to -42.24 kJ/mol, which prove that P1 was chemically adsorbed onto the mild steel surface.

3.3. Quantum chemical calculations

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

Popular qualitative chemical concepts such as electronegativity [27, 28] (χ) and hardness [29] (η) have been provided with rigorous definitions within the purview of conceptual density functional theory [30-32] (DFT). Electronegativity is the negative of chemical potential defined [33] as follows for an N-electron system with total energy E and external potential $v(\vec{r})$

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \qquad \textbf{(7)}$$

μ is the Lagrange multiplier associated with the normalization constraint of DFT [34, 35].
Hardness (η) is defined [36] as the corresponding second derivative,

$$\eta = -\left(\frac{\partial^2 E}{\partial N}\right)_{v(r)} = -\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \quad \mathbf{(8)}$$

Using a finite difference method, working equations for the calculation of χ and η may be given as [37]:

$$\chi = \frac{I+A}{2} \quad \mathbf{(9)}$$

$$\eta = \frac{I-A}{2} \quad \mathbf{(10)}$$

Where I = -E_{HOMO} and A= -E_{LUMO} are the ionization potential and electron affinity respectively.
Local quantities such as Fukui function f(r) defined the reactivity/selectivity of a specific site in a molecule. The Fukui function is defined as the first derivative of the electronic density q(r) of a system with respect to the number of electrons N at a constant external potential v(r) [38].

$$f(r) = \left[\frac{\partial \rho(r)}{\partial N}\right]_{v(r)} = \left[\frac{\delta \mu}{\delta v(r)}\right]_N \mathbf{(11)}$$

Using left and right derivatives with respect to the number of electrons, electrophilic and nucleophilic Fukui functions for a site k in a molecule can be defined [39].

$f_k^+ = P_k(N+1) - P_k(N) \quad for\ nucleophilic\ attack$**(12a)**
$f_k^- = P_k(N) - P_k(N-1) \quad for\ electrphilic\ attack$**(12b)**
$f_k^+ = [P_k(N+1) - P_k(N-1)]/2 \quad for\ radical\ attack$**(12c)**

where, $P_k(N)$, $P_k(N+1)$ and $P_k(N-1)$ are the natural populations for the atom k in the neutral, anionic and cationic species respectively.
The fraction of transferred electrons ΔN was calculated according to Pearson theory [40]. This parameter evaluates the electronic flow in a reaction of two systems with different electronegativities, in particular case; a metallic surface (Fe) and an inhibitor molecule. ΔN is given as follows:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \mathbf{(13)}$$

whereχFe and χinh denote the absolute electronegativity of an iron atom (Fe) and the inhibitor molecule, respectively; ηFe and ηinh denote the absolute hardness of Fe atom and the inhibitor molecule, respectively. In order to apply the eq. 13 in the present study, a theoretical value for the electronegativity of bulk iron was used χFe = 7 eV and a global hardness of ηFe = 0, by assuming that for a metallic bulk I = A because they are softer than the neutral metallic atoms [40].
The electrophilicity has been introduced by Sastri et al. [41], is a descriptor of reactivity that allows a quantitative classification of the global electrophilic nature of a compound within a relative scale. They have proposed the ω as a measure of energy lowering owing to maximal electron flow between donor and acceptor and ω is defined as follows.

$$\omega = \frac{\chi^2}{2\eta} \mathbf{(14)}$$

The Softness σ is defined as the inverse of the η [42]

$$\sigma = \frac{1}{\eta} \mathbf{(15)}$$

The FMOs (HOMO and LUMO) are very important for describing chemical reactivity. The HOMO containing electrons, represents the ability (E_{HOMO}) to donate an electron, whereas, LUMO haven't not electrons, as an electron acceptor represents the ability (E_{LUMO}) to obtain an electron. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity, optical polarizability and chemical hardness–softness of a compound [43]. Firstly, in this study, we calculated the HOMO and LUMO orbital energies by using B3LYP method with 6-31G(d,p). All other calculations were performed using the results with some assumptions. The higher values of E_{HOMO} indicate an increase for the electron donor and this means a better inhibitory activity with increasing adsorption of the inhibitor on a metal surface, where as E_{LUMO} indicates the ability to accept electron of the molecule. The adsorption ability of the inhibitor to the metal surface increases with increasing of E_{HOMO} and decreasing of E_{LUMO}. The HOMO and LUMO orbital energies and image of **P1** were performed and were shown in Table 4 and Figure 5.High ionization energy (I= 6.741 eV, I= 6.940 eV in gas and aqueous phases respectively) indicates high stability [44], the number of electrons transferred (ΔN) was also calculated and tabulated in Table 5. The $\Delta N < 3.6$ indicates the tendency of a molecule to donate electrons to the metal surface [45-46].

Table 4. Quantum chemical descriptors of the studied inhibitor at B3LYP/6-31G(d,p) in gas, G and aqueous, A phases.

	Phase	
Prameters	**Gas**	**Aqueous**
Total Energy***TE* (eV)**	-16537.4	-16537.9
E_{HOMO} (eV)	-6.741	-6.940
E_{LUMO} (eV)	0.007	0.110
Gap**ΔE (eV)**	6.748	7.050
Dipole moment**μ (Debye)**	5.761	7.773
Ionisation potential**I**(eV)	6.741	6.940
Electron affinity **A**	-0.007	-0.110
Electronegativityχ	3.367	3.415
Hardnessη	3.374	3.525
Electrophilicity indexω	1.680	1.654
Softnessσ	0.296	0.283
Fractions of electron transferredΔN	0.538	0.508

The calculated values of the f_k^+ for all inhibitors are mostly localized on the benzodiazepine ring. Namely C_3, C_6, O_{16} and O_{20}, indicating that the benzodiazepine rings will probably be the favorite site for nucleophilic attacks [47-48]. The results also show that O_{16} atom is suitable site to undergo both nucleophilic and electrophilic attacks, probably allowing them to adsorb easily and strongly on the mild steel surface.

Table 5. Pertinent natural populations and Fukui functions of the studied inhibitors calculated at B3LYP/6-31G(d,p) in gas, G and aqueous, A phases.

Atom k	*phase*	*P(N)*	*P(N+1)*	*P(N-1)*	f_k^+	f_k^-	f_k^0
C_1	G	5.8568	5.8932	5.8010	0.0364	0.0558	0.0461
	A	5.8770	5.9079	5.7651	0.0308	0.1120	0.0714
C_2	G	5.9014	5.8931	5.8010	-0.0082	0.1004	0.0461
	A	5.8771	5.9079	5.7651	0.0308	0.1120	0.0714
C_3	G	6.3288	6.4038	6.2413	0.0750	0.0875	0.0813
	A	6.2456	6.4156	6.2492	0.1701	-0.0037	0.0832
C_6	G	6.2490	6.4038	6.2413	0.1548	0.0078	0.0813
	A	6.2456	6.4156	6.2492	0.1701	-0.0037	0.0832
O_{16}	G	8.5872	8.6753	8.4635	0.0881	0.1236	0.1059
	A	8.6337	8.7045	8.5284	0.0709	0.1052	0.0880
O_{20}	G	8.5229	8.6753	8.4636	0.1524	0.0593	0.1058
	A	8.6337	8.7045	8.5284	0.0708	0.1053	0.0880

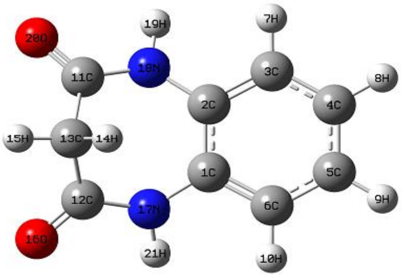
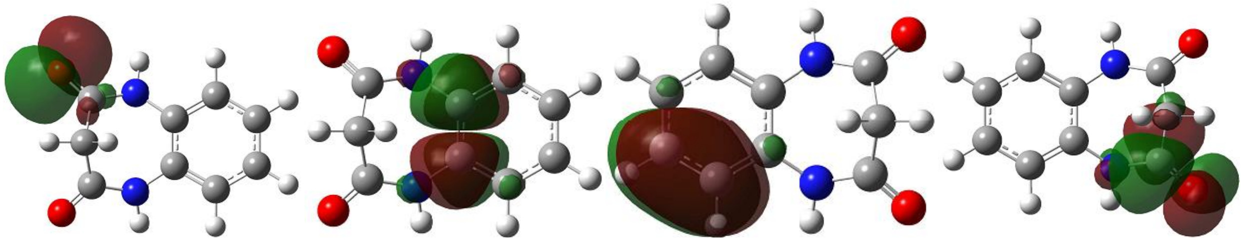


Fig. 5. Optimized molecular structure at B3LYP/6-31G(d,p) level of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1).

After the analysis of the theoretical results, we can say that the molecule **P1** have a non-planar structure. In fact, the CH_2 group is almost perpendicular to the benzodiazepine core.



HOMO (G) LUMO (G) HOMO (A) LUMO (A)

Figure 6. The HOMO and the LUMO electrons density distributions of the studied inhibitors computed at B3LYP/6-31G (d,p) level in gas and aqueous phases.

Conclusions

1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1) shows good inhibition properties for the corrosion of mild steel in 1 M HCl solutions and the inhibition efficiency increases with increasing the concentration of the inhibitor. Tafel polarization measurements show that P1 is mixed-type inhibitor. Based on the properties of impedance diagrams (EIS), one equivalent structure model was selected which could fit the experimental data very well. The inhibiting efficiencies obtained by polarization, EIS and weight loss measurements are in good agreement. The adsorption of 1H-benzo[b][1,4]diazepine-2,4(3H,5H)-dione (P1)on the mild steel/1 M HCl interface obeys the Langmuir adsorption isotherm model. Theoretical calculations were in full agreement with the experimental results and show that the P1 ability to donate electrons lead to its strong adsorption on metal surface.

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