

## **1,2-Diaminoanthraquinone as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid: Weight Loss and Quantum Chemical Study**

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The corrosion inhibition and adsorption processes of 1,2-diaminoanthraquinone (DAQ) on mild steel in HCl was studied at different temperatures (303 – 333 K) by means of weight loss measurement and UV-visible spectrophotometric methods. The results indicate that the studied compound exhibits good performance as inhibitor for mild steel corrosion in 1 M HCl. The inhibition efficiency increases with decreasing temperature and increasing concentration of inhibitor. It has been determined that the adsorption of DAQ on mild steel obeys the Temkin adsorption isotherm at all studied temperatures with negative values of  $\Delta G^{\circ}_{\text{ads}}$ , suggesting a stable and a spontaneous inhibition process. Mechanism of physical adsorption is proposed from the values of  $E_a$  and  $\Delta G^{\circ}_{\text{ads}}$  obtained. The UV-visible absorption spectra of the solution containing the inhibitor after the immersion of mild steel specimen indicate the formation of a DAQ-Fe complex. Quantum chemical approach was further used to calculate some electronic properties of the molecule in order to ascertain any correlation between the inhibitive effect and molecular structure of DAQ.

**Keywords:** 1,2-diaminoanthraquinone (DAQ); adsorption isotherm, Density Functional Theory (DFT), hydrochloric acid, mild steel, corrosion inhibition.

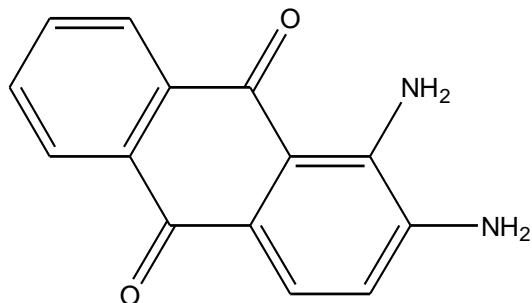
### **1. INTRODUCTION**

Corrosion of mild steel is a fundamental academic and industrial concern that has received considerable amount of attention [1]. However, most equipment in industries is usually corroded owing to the general aggression of acid solutions. Some of the important fields of application of acid

solutions in industries being acid pickling of iron and steel, chemical cleaning, ore production and oil well acidification. Thus, the use of inhibitors is one of the most practical methods for protection against corrosion in acidic media [2].

Organic compounds have long been known to inhibit the corrosion of mild steel in acidic media. Organic compounds previously studied as inhibitors include triazole derivatives [2], bipyrazolic derivatives [3], aromatic hydrazides [4], organic dyes [5,6], poly(4-vinylpyridine) [7] and thiosemicarbazide [8]. These compounds can adsorb onto the mild steel surface and block active sites, thus decreasing the corrosion rate. Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur, and oxygen atoms. Among them, nitrogen-containing heterocyclic compounds are considered to be effective corrosion inhibitors on steel in acid media [9]. N-heterocyclic compound inhibitors act by adsorption on the metal surface, and the adsorption as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures.

Thus, the inhibitory effect of 1,2-diaminoanthraquinone on mild steel corrosion in 1 M HCl at 303 -333 K was studied by weight loss as well as by quantum chemical studies. The inhibitor adsorption mechanism was studied, and the thermodynamic functions for the dissolution and adsorption processes were calculated and discussed. The choice of this compound was also based on molecular structure considerations, i.e., this is an organic compound with several adsorption centres. The molecular structure of 1,2-diaminoanthraquinone is as shown below:



**Figure 1.** The chemical structure of 1,2-diaminoanthraquinone (DAQ)

## 2. EXPERIMENTAL METHOD

### 2.1. Material

The chemical composition of mild steel samples used [9] is shown in Table 1.

The mild steel sheet was mechanically press-cut into coupons of dimension 5cm x 4cm. These coupons were used as supplied without further polishing but were however ground with SiC abrasive paper, degreased in absolute ethanol, dried in acetone, weighed and stored in a moisture free desiccator prior to use [10].

**Table 1.** Chemical Composition of Mild Steel Samples (Wt %).

C	0.17
Si	0.26
Mn	0.46
P	0.0047
S	0.017
Fe	Bal.

## 2.2. Solutions

1 M HCl solution was prepared by dilution of 98% HCl (Analytical grade) using distilled water. 1,2-diaminoanthraquinone was added to the acid in concentrations ranging from 0.2  $\mu\text{M}$  to 1.0  $\mu\text{M}$  and the solution in the absence of 1,2-diaminoanthraquinone was taken as blank for comparison. Tests were conducted under total immersion conditions in 100 ml of test solutions maintained at 303 – 333 K. The pre-cleaned and weighed coupons were immersed in beakers containing the test solutions.

To determine weight loss with respect to time, the coupons were retrieved from test solutions at 2hrs interval progressively for 10hrs, immersed in 20% NaOH solution containing 200g $\text{l}^{-1}$  of zinc dust, scrubbed with bristle brush, washed in distilled water, dried in acetone and re-weighed. The weight loss was taken to be the difference between the weight of the coupons at a given time and its initial weight of the test coupon determined using LP 120 digital balance with sensitivity of  $\pm 1$  mg.

## 2.3. Gravimetric measurements

The apparatus and procedure followed for the weight loss measurements were as previously reported [11-15]. The corrosive concentration was kept at 1 M HCl and the volume of the test solution used was 100 mL. All tests were made in aerated solutions. The difference between the weight at a given time and the initial weight of the coupons was taken as the weight loss which was used to compute the corrosion rate given by [9]:

$$\rho = \frac{\Delta W}{At} \quad (1)$$

Where,  $\Delta W$  is the weight loss,  $A$  is the total area of the mild steel coupon,  $t$  is the corrosion time and  $\rho$  is the corrosion rate.

$$\text{Surface coverage, } \theta = \frac{(\rho_1 - \rho_2)}{\rho_1} \quad (2)$$

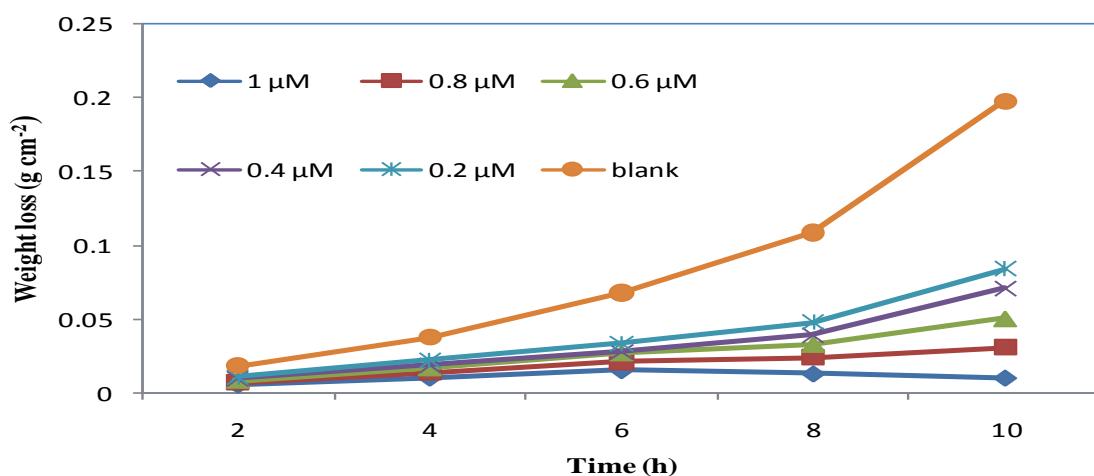
$$\text{Inhibition efficiency, } \% I = \left( \frac{\rho_1 - \rho_2}{\rho_1} \right) \times 100 \quad (3)$$

Where  $\rho_1$  and  $\rho_2$  are the corrosion rates of the mild steel in 1 M HCl (blank) in the absence and presence of inhibitor respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Weight loss, corrosion rate and inhibition efficiency

The weight loss (gravimetric measurements) for the mild steel in 1 M HCl containing different concentrations of DAQ as function of time at 303 K is presented in Fig. 2.



**Figure 2.** Variation of weight loss versus time (h) for mild steel corrosion in 1 M HCl in the absence and presence of different concentrations of 1,2-diaminoanthraquinone at 303 K.

The results show that weight loss increase with increase in time but decrease with increase in concentration of the 1,2-diaminoanthraquinone (DAQ). The decrease is due to the inhibitive effects of the inhibitor and these effects increase with increase in concentration of the inhibitor. The values of corrosion rate, surface coverage ( $\theta$ ) and inhibition efficiency from weight loss measurements at different concentrations of the studied inhibitor after 10hrs immersion at 303-333 K are summarized in Table 2.

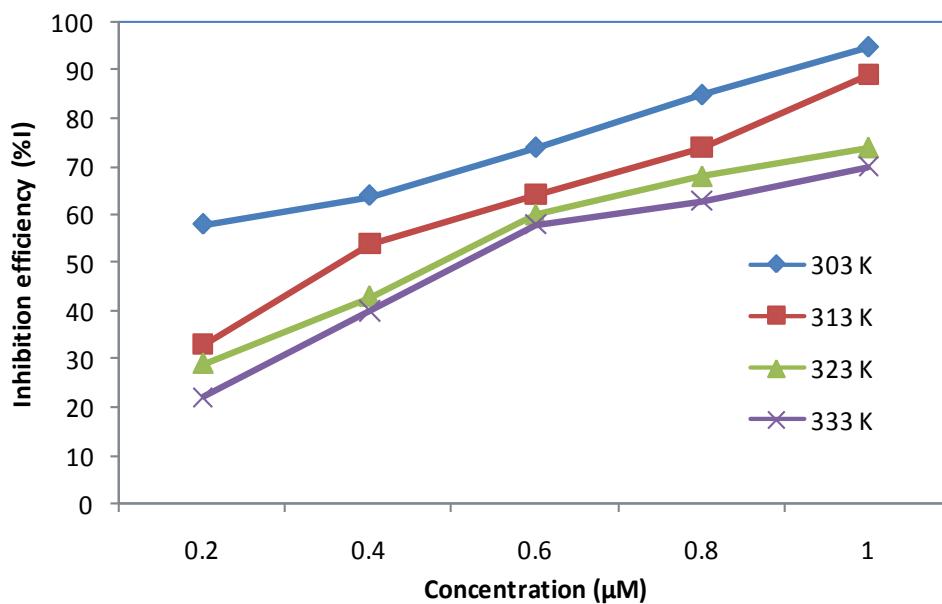
It is evident from this table that the inhibition efficiency (%I) increased with increasing inhibitor concentration, reaching a maximum of 95.0%. This may be due to the adsorption of 1,2-diaminoanthraquinone onto the mild steel surface through non-bonding electron pairs of nitrogen and oxygen atoms as well as the  $\pi$ -electrons of the aromatic rings. The high inhibitive performance of 1,2-diaminoanthraquinone suggests a higher bonding ability of the inhibitor to the mild steel surface. Similar observation has been reported elsewhere [16].

**Table 2.** Corrosion parameters for mild steel in 1 M HCl in the absence and presence of different concentrations of 1,2-diaminoanthraquinone at different temperatures

Concentration of 1,2diaminoanthraquinone ( $\mu\text{M}$ )	Corrosion rate, inhibition efficiency (% I) and degree of surface coverage ( $\theta$ )											
	303 K			313 K			323 K			333 K		
	$a \times 10^{-4}$	b	c	$a \times 10^{-4}$	b	c	$a \times 10^{-4}$	b	c	$a \times 10^{-4}$	b	c
Blank	9.89	-	-	10.1	-	-	11.3	-	-	15.1	-	-
0.2	4.20	58	0.58	6.74	33	0.33	8.07	29	0.29	11.8	22	0.22
0.4	3.55	64	0.64	4.64	54	0.54	6.40	43	0.43	9.13	40	0.40
0.6	2.53	74	0.74	3.53	64	0.64	4.50	60	0.60	6.41	58	0.58
0.8	1.51	85	0.85	2.66	74	0.74	3.64	68	0.68	5.60	63	0.63
1.0	0.52	95	0.95	1.15	89	0.89	2.98	74	0.74	4.47	70	0.70

(a) Corrosion rate obtained from equation (1); (b) Inhibition efficiency (%I) obtained using equation (2); (c) Degree of surface coverage ( $\theta$ ) obtained using equation (3).

The inhibition efficiency as a function of concentration is shown in Fig. 3. The result shows that as the inhibitor concentration increases, the corrosion rate decreases and therefore the inhibition efficiency increases.

**Figure 3.** Variation of Inhibition efficiency (%I) against concentrations of 1,2-diaminoanthraquinone at different temperatures.

This implies that this inhibitor act through adsorption on the mild steel surface and formation of a barrier layer between the metal and the corrosive medium. Thus, in order to confirm the adsorption

of 1,2-diaminoanthraquinone on mild steel surface, adsorption isotherms were studied which provided basic information on the interaction of inhibitor and metal surface.

The degree of surface coverage values ( $\theta$ ), at different inhibitor concentrations in 1 M HCl was evaluated from weight loss measurements at 303–333K and tested graphically for fitting to a suitable adsorption isotherm.

### 3.2. Adsorption /thermodynamics studies

It is important to determine empirically which adsorption isotherm fits best to the surface coverage data in order to use the corrosion rate measurements to calculate the thermodynamics parameters pertaining to inhibitor adsorption. The models considered were [6, 17-21]:

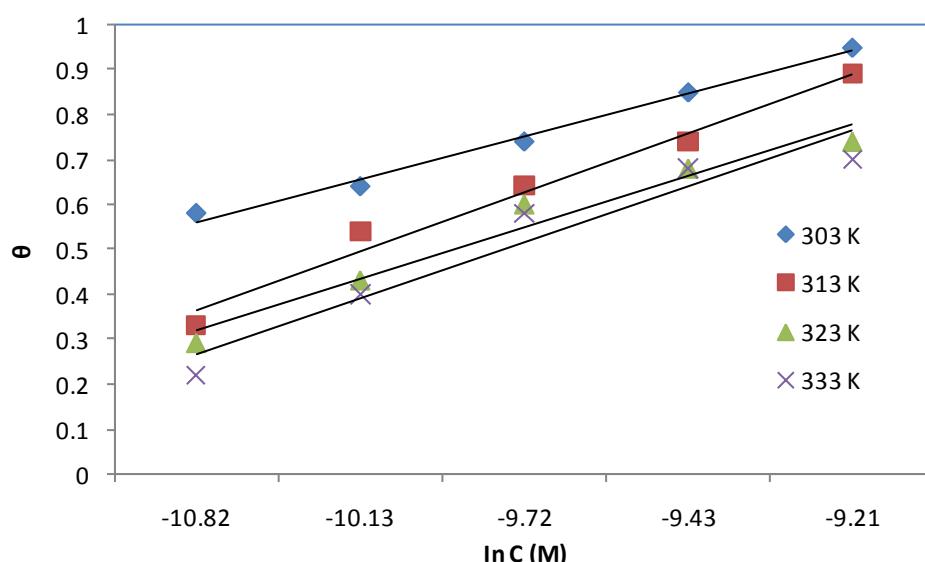
$$\text{Temkin isotherm: } \exp(f\theta) = K_{ads}C \quad (4)$$

$$\text{Langmuir isotherm: } \theta = K_{ads}C \quad (5)$$

$$\text{El-Awady isotherm: } \log \frac{\theta}{1-\theta} = \log K_{ads}^{-1} + y \log C \quad (6)$$

$$\text{Freundlich isotherm: } \log \theta = \log K_{ads} + n \log C \quad (7)$$

Where  $K_{ads}$  is the equilibrium constant of the adsorption process,  $C$  the inhibitor concentration and  $f$  the factor of energetic inhomogeneity. The best fitted straight line was obtained from the plot of surface coverage ( $\theta$ ) versus logarithmic of inhibitor concentration ( $\log C$ ), Fig. 4.



**Figure 4.** Temkin adsorption isotherm plot as  $\theta$  versus  $\ln C (M)$  for 1,2-diaminoanthraquinone at 303 – 333 K.

The experimental data fit best the Temkin adsorption isotherm as the correlation coefficients ( $R^2$ ) were in the range  $0.9900 \geq R^2 \geq 0.9260$ . This suggested that the adsorption of 1,2-diaminoanthraquinone on the metal surface obeyed the Temkin adsorption isotherm. Temkin adsorption isotherm is given [22];

$$\exp(-2a\theta) = K_{ads}C \quad (8)$$

Where, 'a' is molecular interaction parameter. The calculated values of molecular interaction parameter 'a' and the equilibrium constant of adsorption process,  $K_{ads}$  deduced from Temkin adsorption plot (Fig. 4) is also shown in Table 3. The parameter 'f' is defined as:

$$f = -2a \quad (9)$$

**Table 3.** Adsorption parameters from Temkin isotherm for mild steel coupons in 1 M HCl containing different concentration at 303-333 K.

Inhibitor	Temperature (K)	Adsorption parameters				
		$K_{ads}$ (mol/L)	f	a	$-\Delta G(kJ/mol)$	$R^2$
DAQ	303	6.40	10.53	-5.27	22.50	0.990
	313	5.80	7.58	-3.79	15.03	0.979
	323	5.84	8.70	-4.35	15.52	0.962
	333	3.19	8.07	-4.04	14.33	0.926

Where  $f$  is the heterogeneous factor of the metal surface describing the molecular interactions in the adsorption layer. Eq. (9) clearly shows that the sign between  $f$  and  $a$  is reverse, that is, if  $a < 0$ , then  $f > 0$ ; if  $a > 0$ , then  $f < 0$ . Accordingly, if  $f > 0$ , mutual repulsion of molecules occurs and if  $f < 0$  attraction takes place [23].

It is a known fact that  $K_{ads}$  denotes the strength between adsorbate and adsorbent. Large values of  $K_{ads}$  imply more efficient adsorption and hence better inhibition efficiency. It is clear from Table 3 that values of  $K_{ads}$  are very low indicating weak interaction between the inhibitor and the mild steel surface. It seems therefore, that electrostatic interaction (Physisorption) between the inhibitor molecules existing as cations should prevail over molecular interaction which often results in strong interactions (Chemisorption) [22].

The equilibrium constant of adsorption,  $K_{ads}$  is related to the standard free energy of adsorption ( $\Delta G_{ads}$ ), with the following equation [4].

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \quad (10)$$

Where R is the molar gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution expressed in molar.

Rearranging the Equation (10) gives

$$\log K_{ads} = 1.744 - \frac{\Delta G_{ads}^o}{2.303RT} \quad (11)$$

From where, the standard free energy of adsorption ( $\Delta G_{ads}^o$ ) was calculated (Table 3). The negative values of the  $\Delta G_{ads}^o$  reflect the spontaneity of the adsorption process and stability of the adsorbed layer on the mild steel surface.

Generally, values of  $\Delta G_{ads}^o$  up to  $-20\text{ kJ mol}^{-1}$  are consistent with electrostatic interactions between the charged molecules and the metal ( physisorption) while those around  $-40\text{ kJ mol}^{-1}$  or higher are associated with chemisorptions as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond ( chemisorptions) [23]. One can see that the calculated  $\Delta G_{ads}^o$  values are less than  $-20\text{ kJ mol}^{-1}$ , indicating, therefore that the adsorption mechanism of the 1,2-diaminoanthraquinone on mild steel in 1 M HCl solution was typical of physisorption.

### 3.3. Temperature Effect

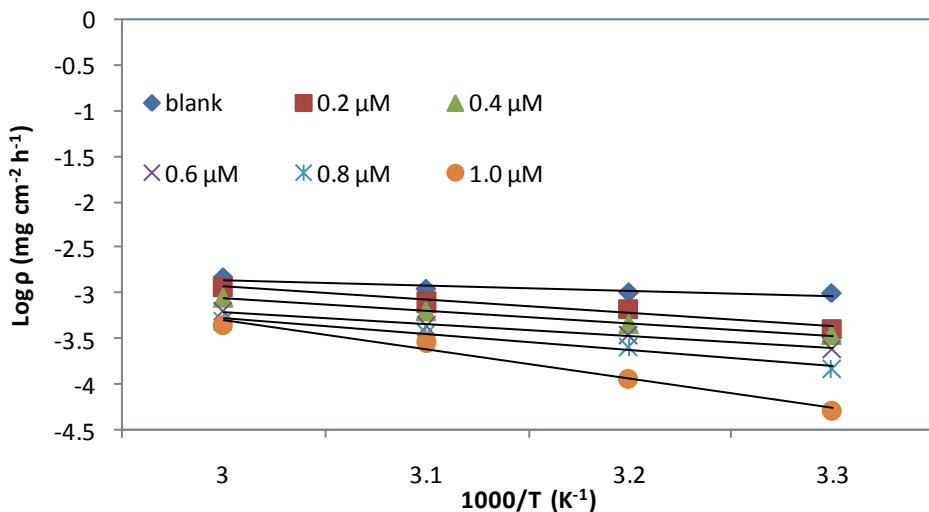
The effect of temperature on the corrosion rate of mild steel in 1 M HCl solution in the absence and presence of 0.2  $\mu\text{M}$  to 1.0  $\mu\text{M}$  of 1,2-diaminoanthraquinone was studied at different temperatures (303-333 K) by weight loss measurements. The effect of temperature on the inhibited acid-metal reaction is very complex, because many changes occur on the metal surface such as rapid etching, desorption of inhibitor and the inhibitor itself may undergo decomposition [24]. Table 2 shows that the Inhibition efficiency decreases as the temperature increases and with decrease in concentrations of studied inhibitor.

Fig. 3 shows the variation of percentage inhibition efficiency with temperature. It is clear from the figure that percentage inhibition efficiency increases with DAQ concentration but decreases with increase in temperature. This may be probably due to increased rate of desorption of DAQ from the mild steel surface at higher temperature [25-26].

In acidic solution, the corrosion rate is related to temperature by the Arrhenius equation [27].

$$\log \rho = \log A - \frac{E_a}{2.303RT} \quad (12)$$

Where  $\rho$  is the corrosion rate determined from the weight loss measurement,  $E_a$  is the apparent activation energy,  $A$  is the Arrhenius constant,  $R$  the molar gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $T$  is the absolute temperature. The apparent activation energy,  $E_a$  was determined from the slopes of  $\log \rho$  versus  $1/T$  graph depicted in Fig. 5.



**Figure 5.** Arrhenius plot as  $\log \rho$  versus  $1/T$  for mild steel coupons in 1M HCl containing different concentration of 1,2-diaminoanthraquinone.

The values of activation energies were calculated and given in Table 4.

**Table 4.** Activation parameters for mild steel coupons in 1M HCl containing different concentration of 1,2-diaminoanthraquinone at 303-333 K.

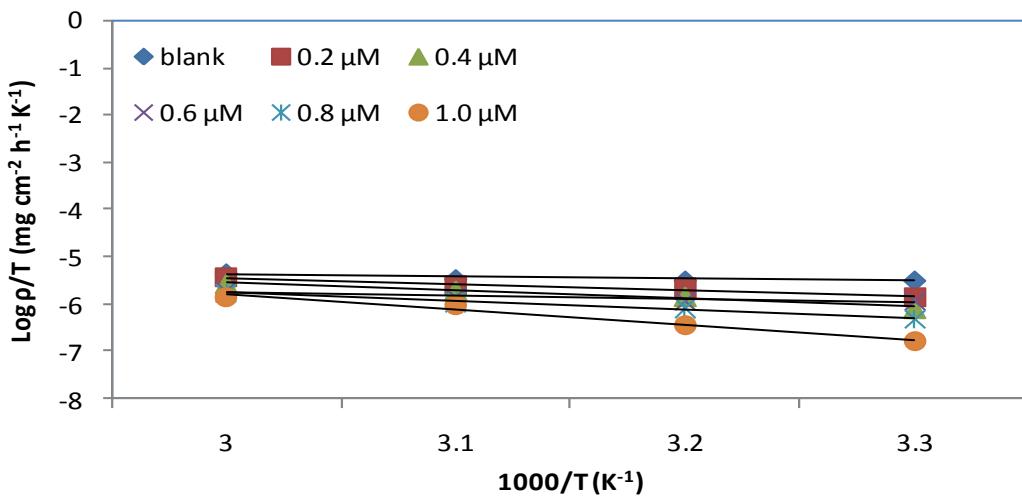
Concentration	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H^*$ (kJ/mol)	$-\Delta S^*$ (J/molK <sup>-1</sup> )
<b>Blank</b>	1.11	0.92	299.6
<b>0.2 μM</b>	2.62	2.49	299.8
<b>0.4 μM</b>	2.74	3.24	300.5
<b>0.6 μM</b>	2.85	5.96	302.9
<b>0.8 μM</b>	3.26	5.97	304.8
<b>1.0 μM</b>	6.13	5.99	304.9

These values indicate that the presence of 1,2-diaminoanthraquinone increases the activation energy of the metal dissolution reaction. The increase in  $E_a$  is proportional to the inhibitor concentration. The increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature and a corresponding increase in corrosion rates due to the fact that greater area of metal is exposed to the acid environment [28]. The adsorption of the studied inhibitor is assumed to occur on the higher energy sites and the presence of the inhibitor, which results in the blocking of the active sites, must be associated with an increase in the activation energy of mild steel corrosion in the inhibited state [6]. The higher value of

$E_a$  in the presence of inhibitor compared to that in its absence and the decrease in the Inhibition efficiency with rise in temperature is interpreted as an indication of physisorption. The values of enthalpy of activation  $\Delta H^*$  and entropy of activation,  $\Delta S^*$  were obtained from the transition state equation [8].

$$\rho = \left( \frac{RT}{Nh} \right) \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( -\frac{\Delta H^*}{RT} \right) \quad (13)$$

Where  $\rho$  is the corrosion rate,  $h$  is the Planck's constant ( $6.6261 \times 10^{-34}$  Js);  $N$  is the Avogadro's number ( $6.02252 \times 10^{23}$  mol $^{-1}$ );  $T$  is the absolute temperature and  $R$  is the universal gas constant. A plot of  $\log(\rho/T)$  as a function of  $1/T$  (Fig. 6) was made for mild steel corrosion in 1 M HCl in the absence and presence of different concentrations of DAQ.



**Figure 6.** Transition State plot as  $\log(\rho/T)$  versus  $1/T$  for mild steel coupons in 1 M HCl containing different concentration of 1,2-diaminoanthraquinone.

Straight lines were obtained with slope of  $(\Delta H^*/2.303R)$  and an intercept of  $[\log(R/Nh) + (\Delta S^*/2.303R)]$  from which the values of  $\Delta H^*$  and  $\Delta S^*$ , respectively, were computed and listed also in Table 4. Examination of these data reveals that the  $\Delta H^*$  values for dissolution reaction of mild steel in 1 M HCl in the presence of DAQ are higher ( $2.49 - 5.99$  kJ mol $^{-1}$ ) than that in the absence of DAQ ( $0.92$  kJ mol $^{-1}$ ). The positive sign of  $\Delta H^*$  show the endothermic nature of the solution process suggesting that the dissolution of mild steel is slow [8, 29], which indicates that inhibition efficiencies decrease with increase in temperature. It is also clear from Table 4 that  $E_a$  and  $\Delta H^*$  increase with increase in DAQ concentration.

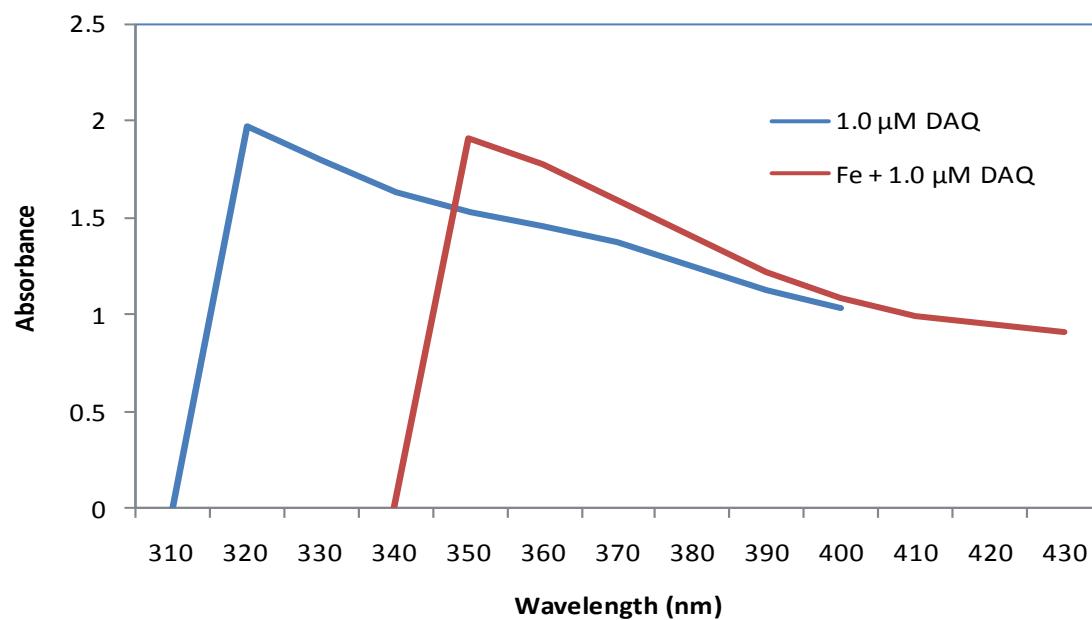
Entropy of activation,  $\Delta S^*$  remains almost constant with increasing DAQ concentration (Table 4) and their values were negative both in the uninhibited and inhibited systems. The entropy of inhibitor adsorption ( $\Delta S_{ads}^*$ ) was negative because inhibitor molecules, freely moving in the bulk solution were adsorbed in an orderly fashion onto the mild steel surface, resulting in an increase in

entropy. This implies that the activated complex in the rate determining step represents an association rather than a dissolution step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [30].

### 3.4. UV-visible spectroscopy

The absorption of monochromatic light is a suitable method for identification of complex ions; the absorption of light is proportional to the concentration of the absorbing species [8]. Since there is often a certain quantity of metal cation in the solution that is first dissolved from the metal surface, such procedures were conducted in the present work to confirm the possibility of the formation of [DAQ-Fe<sup>2+</sup>] complexes as described in other several publications [31-34]. Furthermore, the change in position of the absorbance maximum and change in the value of absorbance indicate the formation of a complex between two species in solution [8].

For routine analysis a simple conventional technique based on UV-visible absorption spectra obtained from 1 M HCl solution containing 1.0 μM 1,2-diaminoanthraquinone before (blue) and after (red) 3 days of mild steel immersion is shown in Fig. 7.



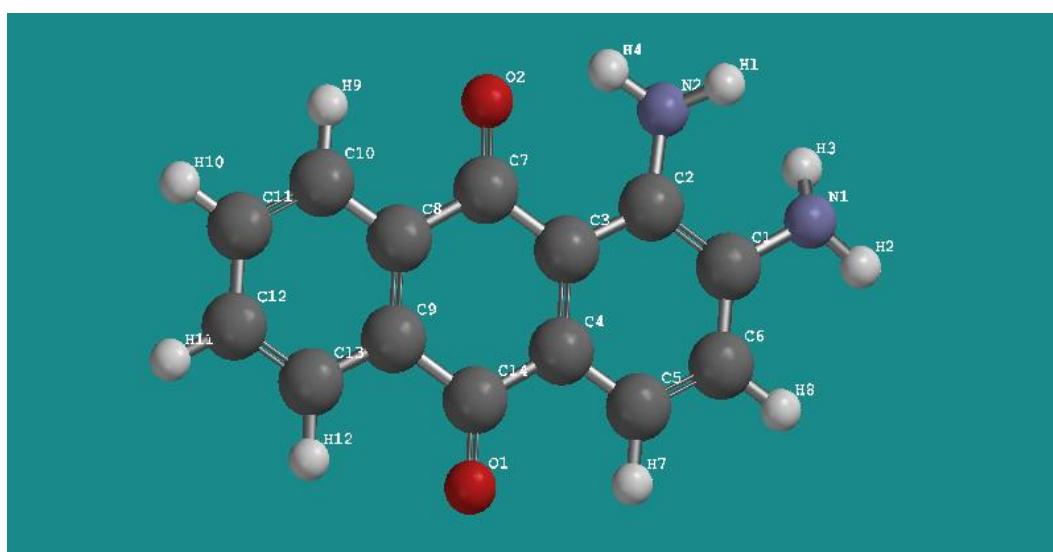
**Figure 7.** UV-Visible spectra of the solution containing 1 M HCl and (1.0 μM) 1,2-diaminoanthraquinone before (blue) and after (red) three days of mild steel immersion.

The absorption spectrum of the solution containing 1.0 μM 1,2-diaminoanthraquinone before the mild steel immersion shows a band of shorter wavelength while that of 3 days of steel immersion shows a band of longer wavelength (Fig. 7). The electronic absorption spectra of DAQ before the steel immersion display a main visible band at 340 nm. This band may be assigned to  $\pi-\pi^*$  transition involving the whole electronic structure system of the compound with a considerable charge transfer

character [35]. After three days of steel immersion (Fig. 7), it is clearly seen that the band maximum underwent a blue shift, suggesting the interaction between DAQ and  $\text{Fe}^{2+}$  ions in the solution [8, 36]. Furthermore, there is an increase in the absorbance of this band. It is clear that there was no significant difference in the shape of the spectra before and after the immersion of DAQ showing a possibility of weak interaction between DAQ and mild steel (Physisorption) [36]. This indicates that the amine and carbonyl groups are weakly held up in the complex with iron [11]. These experimental findings provide a strong evidence for the possibility of the formation of a complex between  $\text{Fe}^{2+}$  cation and the studied inhibitor in 1 M HCl solution [12].

### 3.5 Quantum Chemical Studies

Quantum chemical calculations have proved to be a very powerful tool for studying corrosion inhibition mechanism [13]. Thus, a theoretical study was undertaken to observe the possible physical characters which could contribute to inhibition. Recently, the density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/surface mechanism and to describe the structural nature of the inhibitor on the corrosion process [36 – 39]. Thus in the present investigation, quantum chemical calculation using DFT was employed to explain the experimental results obtained in this study and to further give insight into the inhibition action of DAQ on the mild steel surface.



**Figure 8.** DFT-B3LYP Optimized Structure of 1,2-diaminoanthraquinone.

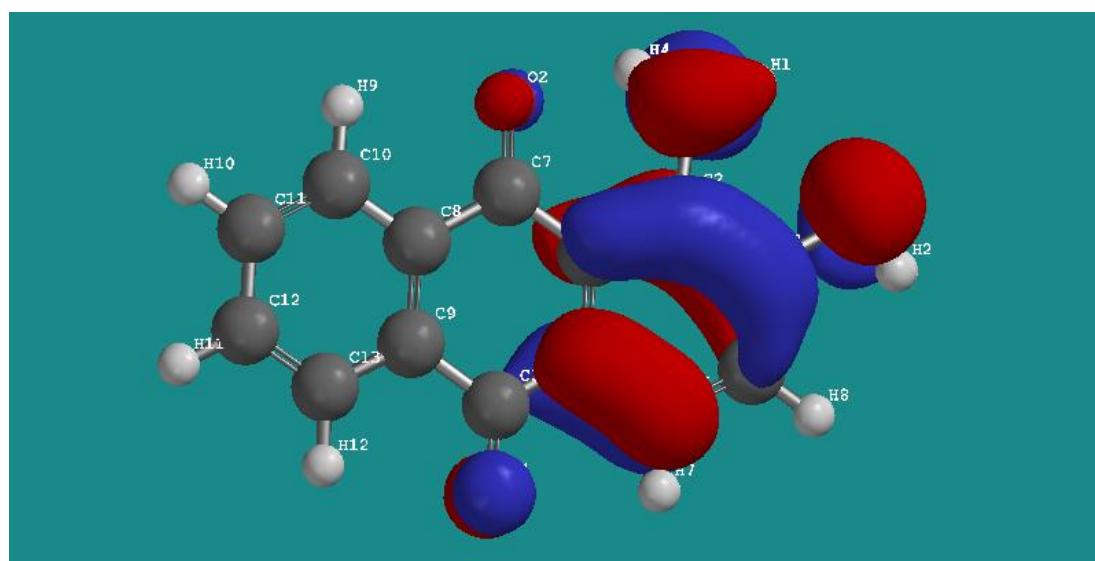
The calculated values of the quantum chemical parameters obtained using the Hartree-fock/Density functional theory (HF-DFT) by Becke 3 Lee Yang Parr (B3LYP) method with 6-31G\* basis set of SPARTAN' 06 V112 program are presented in Table 5. The relation between inhibition efficiency of inhibitor and the calculated quantum chemical parameters like  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , dipole moment and  $E_{\text{LUMO}} - E_{\text{HOMO}}$  ( $\Delta E$ ) were investigated. These parameters provide information about the reactive behavior of molecules. These theoretical parameters were calculated in the neutral as well as

in the protonated form of DAQ in the aqueous phase. The reactive ability of the inhibitor is considered to be closely related to their frontier molecular orbitals, the HOMO and LUMO [36]. The highest occupied molecular orbital (HOMO) is usually the region of high electron density, therefore is often associated with the electron donating ability of the molecule to appropriate acceptor molecules with low-energy empty molecular orbital and thus explains the adsorption on metallic surfaces by way of delocalized pairs of  $\pi$ -electrons.  $E_{LUMO}$ , the energy of the lowest unoccupied molecular orbital signifies the electron receiving tendency of a molecule. The optimized geometry of 1,2-diaminoanthraquinone is shown in Fig. 8.

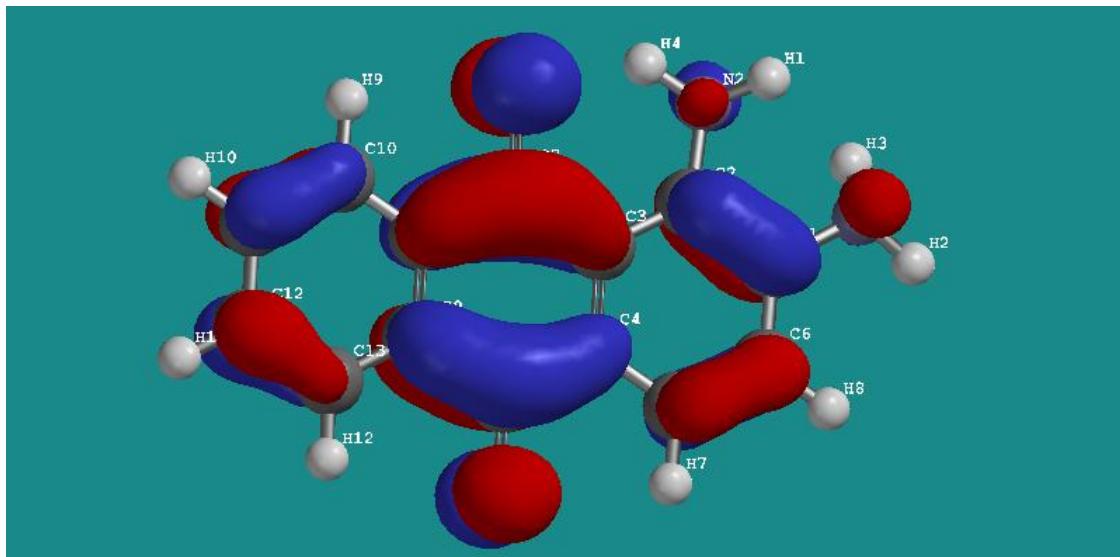
**Table 5.** Quantum chemical parameters obtained by Spartan'06

Quantum chemical parameter	Neutral calculated value	Protonated calculated value
	DAQ	DAQ
$E_{HOMO}$ (eV)	-5.557	-10.167
$E_{LUMO}$ (eV)	-2.469	-6.510
$E_{LUMO} - E_{HOMO}$ (eV)	3.088	3.658
<b>Heat of Formation (kJ/mol)</b>	-799.512	-799.940
CPK area ( $\text{\AA}^2$ )	239.510	244.440
CPK volume ( $\text{\AA}^3$ )	231.150	233.570
Dipole moment(Debye)	2.970	9.710
Molecular weight (amu)	238.246	239.254

As we know, frontier orbital theory is useful in predicting the adsorption centers of the inhibitors responsible for the interaction with surface metal atoms.



**Figure 9.** HOMO electronic density of 1,2-diaminoanthraquinone molecule



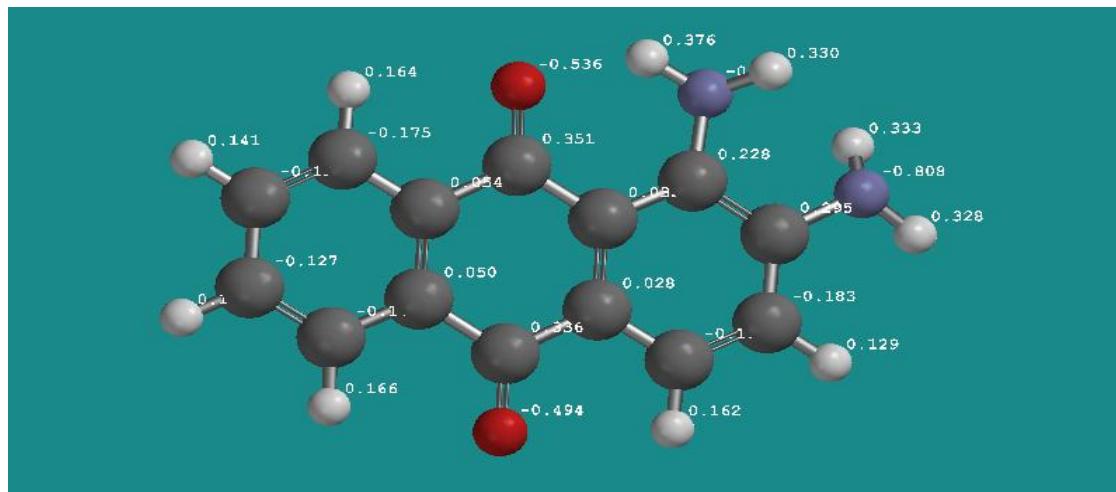
**Figure 10.** LUMO electronic density of 1,2-diaminoanthraquinone molecule

The HOMO and the LUMO population of 1, 2-diaminoanthraquinone are shown in Figs. 9 and 10 respectively. It could also be easily seen that the HOMO were distributed mainly around the benzene ring and the nitrogen atoms of the amine group while the LUMO were distributed on the entire molecule.

Moreover, the gap between the LUMO and HOMO energy levels of the molecule was another important factor that should be considered. It has been reported that excellent corrosion inhibitors are usually those organic compounds that do not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal [14]. It is also well documented in literature that the higher the HOMO energy of the inhibitor, the greater its ability of offering electrons to unoccupied d-orbital of the metal, and the higher the corrosion inhibition efficiency. It is evident from Table 5 that DAQ has the highest  $E_{HOMO}$  in the neutral form and a lower  $E_{HOMO}$  in the protonated form. This means that the electron donating ability of DAQ is weaker in the protonated form. This confirms the experimental results that interaction between DAQ and mild steel is electrostatic in nature (physisorption). In addition, the lower the LUMO energy, the easier the acceptance of electrons from the metal surface, and as the LUMO – HOMO energy gap decreased, the efficiency of inhibitor improved [14]. It is clear from Table 5 that the protonated form of DAQ exhibits the lowest  $E_{LUMO}$ , making the protonated form the most likely form for the interaction of mild steel with DAQ molecule. Low values of the energy gap ( $\Delta E$ ) will provide good inhibition efficiencies, because the excitation energy to remove an electron from the last occupied orbital will be low [40]. A molecule with a low energy gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is termed soft molecule [41]. The adsorption of inhibitor onto a metallic surface occurs at the part of the molecule which has the greatest softness and lowest hardness [42]. Quantum chemical parameters listed in Table 5 indicates that 1,2-diaminoanthraquinone is an efficient inhibitor in HCl which corresponds to the experimental results. The Mulliken charge distribution of 1,2-diaminoanthraquinone is presented in Table 6 and Fig. 11.

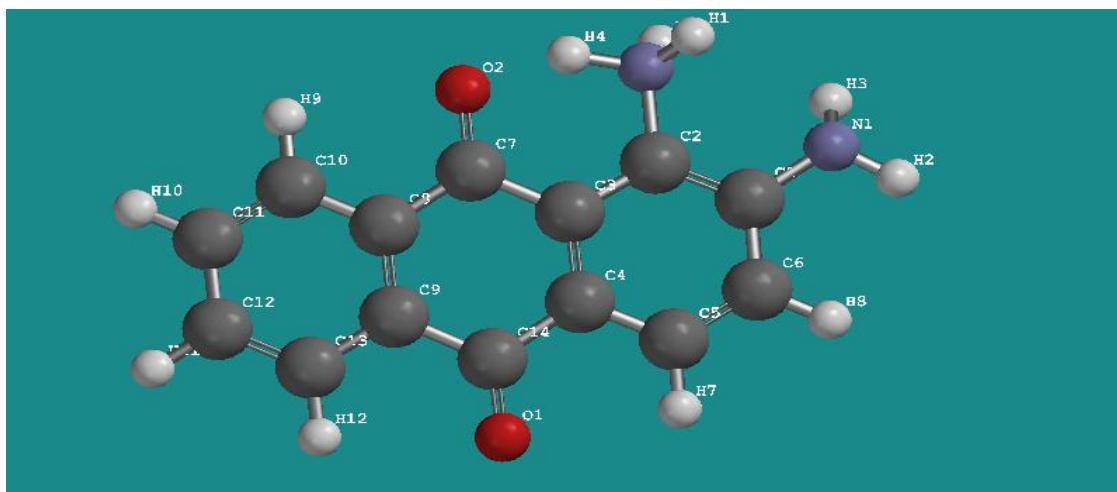
**Table 6.** The atoms in 1,2-diaminoanthraquinone molecule and their Mulliken charges

Atom	Charge
C1	-0.163819
C2	-0.127784
C3	-0.137421
C4	-0.147748
C5	0.266845
C6	0.298287
C7	0.182168
C8	0.557723
C9	0.626860
C10	0.770390
N1	-0.519541
N2	-0.569795
N3	-0.701118
N4	-0.729677
O1	-0.455971
O2	-0.486260

**Figure 11.** Mulliken Charges of the atoms in 1,2-diaminoanthraquinone

It has been reported that the more negative the atomic charges of the adsorbed centre, the more easily the atom donates its electron to the unoccupied orbital of the metal [43]. It is clear from Table 6 and Fig. 11 that nitrogen and oxygen as well as some carbons atoms carries negative charge centers

which could offer electrons to the mild steel surface to form a coordinate bond. It could be readily observed that oxygen, nitrogen atoms and the benzene ring had higher charge densities and might form the adsorption centers.



**Figure 12.** Optimized structure of 1,2-diaminoanthraquinone protonated at N2

In acidic solution, this studied inhibitor can exist as cationic species through the protonation of nitrogen atoms. The protonated compound (Fig. 12) can be adsorbed on the metal surface by means of electrostatic interaction between  $\text{Cl}^-$  (which act as a bridge between the metal surface and the electrolyte) and protonated DAQ. Moreover, the adsorption of this compound on the anodic sites through lone pair of electrons on N atoms and through the  $\pi$ -electrons of the phenyl groups will then reduces the anodic dissolution of mild steel [44].

The dipole moment is another important electronic parameter that results from non-uniform distribution of charges on the various atoms in a molecule. It is mainly used to study the intermolecular interactions involving the Van der Waals type dipole-dipole forces etc, because the larger the dipole moment the stronger will be the intermolecular attraction [41]. The dipole moment of DAQ (Table 5) is highest in the protonated form ( $9.71 \text{ D}$ ;  $32.4 \times 10^{-30} \text{ Cm}$ ), which is higher than that of  $\text{H}_2\text{O}$  ( $\mu = 6.23 \times 10^{-30} \text{ Cm}$ ). The high value of dipole moment probably increases the adsorption between chemical compound and metal surface [45]. The values of dipole moment indicate the possibility of adsorption of studied compound by electron donation to the unfilled orbital of iron. The electronic configuration of iron is  $[\text{Ar}] 4\text{S}^2 3\text{d}^6$ , so 3d orbital is not fully filled with electrons. Accordingly, the adsorption of DAQ molecules can be regarded as a quasi-substitution process between the DAQ compound and water molecules at the mild steel surface [36].

From the above discussion, it could be deduced that 1,2-diaminoanthraquinone interact with the mild steel surface using a number of active centers forming a good protective layer on the mild steel surface, thus retarding further corrosion of the metal in hydrochloric acid solution. It also exists in the cationic form which can interact with mild steel surface by electrostatic attraction.

#### 4. CONCLUSIONS

- Results obtained from the experimental and theoretical data show that 1,2-diaminoanthraquinone (DAQ) acts as an effective inhibitor of mild steel corrosion in 1M HCl.
- The corrosion process was inhibited by adsorption of the DAQ on the steel surface.
- Inhibition efficiency increases with increase in the concentration of 1,2-diaminoanthraquinone but decreases with rise in temperature.
- The adsorption of DAQ on mild steel surface from 1 M HCl obeys the Temkin adsorption isotherm.
- Phenomenon of physical adsorption is proposed from the values of kinetic/thermodynamics parameters ( $E_a$ ,  $\Delta G^{\circ}_{ads}$ ) obtained.
- The UV-Visible studies clearly reveal the formation of complex which may be also responsible for the observed inhibition.
- Quantum chemical calculations show that apart from studied compound molecule adsorbing as cationic species on the mild steel surface, it can also adsorbed as molecular species using oxygen, nitrogen and benzylic carbons as its active centers.

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