Molecular Dynamics and Adsorption Behaviour of 2, 3- Diaminopyridine and 9, 10-Diaminophenanthrene In Neutral and Protonated Forms

K. E. Essien[1*], Okon, O. E[2], I. O. Ekpenyong[3], Effiong, James Okon[4]

[1]*Department of Chemistry, Akwa Ibom State University, P.M.B. 1167, Ikot Akpaden, Akwa Ibom State, Nigeria*

[2,3,4] *Department of Science Technology, Akwa Ibom State Polytechnic, P.M.B. 1101, Ikot Osurua, Akwa Ibom State, Nigeria*

Abstract: **A computational studies on corrosion inhibition potential of 2,3- Diaminopyridine (DAP) and 9,10-Diaminophenanthrene (DAPN) were investigated using density functional theory (DFT) with RHF/STO-6G* method. Interesting results were obtained as the inhibition properties of these compounds correlated with molecular properties. With the aid of quantum chemical parameters such as E_{HOMO}, E_{LUMO}, energy gap, ionization energy, electron affinity, global hardness, global softness, global electrophilicity index, back donation and absolute electronegativity, the corrosion inhibition potentials were predicted. It was observed that the predictive corrosion inhibition potential of DAPN molecule is greater than that of DAP molcule. Nitrogen and carbon atoms were the sites of likely electrophilic attack as shown by high negative mulliken charges of these molecules. The binding sites of DAPN and DAP molecules on the surface of metal were further proven by molecular electrostatic potentials (MEPs).**

Keywords: **corrosion, inhibition, 2,3- Diaminopyridine, 9,10-Diaminophenanthrene, density**

I. INTRODUCTION

Organic inhibitors are prevalence in industry for corrosion prevention of steel and its alloy. These may be due to their availability and eco-friendliness. Corrosion inhibition possesses advantages of economy, high-efficiency and facile-feasibility among other corrosion prevention measures, and has been widely applied in various fields such as petroleum extraction and refining, electric and power construction [1–3]. The large extent of interaction between the inhibitor and the metal surface prove the effectiveness of the inhibitor [4]. The metal surface is covered by a protective barrier against corrosive agent in the environment [5]. The aggressive acid solutions come in direct contact with metals during industrial processes such as metal removal and cleaning, acid descaling and oil well acidizing. In other to inhibit metal corrosion, corrosion inhibitors need to be added to an acid solution before using in any industrial process [6].

Organic compounds are known to be good corrosion inhibitors because of their ability to donate electrons to unoccupied d-orbitals of a metal surface or adsorption sites in the surface of an oxide (Passive) film to form coordinate covalent bonds or may also accept free electrons from metal surface by using their antibonding orbitals to form feedback bonds [7]. However, the formation of a chelate on the metal surface which include the transfer of electrons from the organic compounds to the metal, forming coordinate covalent bonding during such chemical adsorption process are usually promoted by many organic inhibitors. In this way, the metal acts as an electrophile whereas the nucleophile centres of the inhibitors molecules are normally heteroatom with free electron pairs which are readily available for sharing to form a bond [8].

In investigating the mechanism of corrosion inhibition such as quantum chemical calculations, the use of computational method will continue to make great impact in corrosion science research because of the advances in computer softwares [9,10]. Inhibition mechanisms have now been deeply examined through investigation of the structure, electron distribution of molecules onto metal and oxides surfaces. Vosta (1971) introduced quantum chemical method to investigate corrosion inhibition and this founded the field of quantum electrochemistry [9]. The quantum chemical method which was mainly used on exploring and establishing relationship between inhibition efficiency and molecular structure can now be used in defining the interaction between inhibitor molecules and metal surfaces [10,11].

DFT has become a main stay in connecting some empirical concepts in corrosion science with quantum mechanics. A number of chemical concepts have been correlated within the framework of DFT. Density Functional Theory is one of the most important theoretical methods use in explaining the science of solid and chemistry [12]. Due to their accuracy and shorter computational time, DFT methods have become very popular in the last decade.

The aim of the present work is to examine the inhibition ability of 2,3- Diaminopyridine and 9,10-Diaminophenanthrene. The observable inhibitory effect is strengthened by the presence of heteroatoms such as Nitrogen, Oxygen and π-bonds in the aromatic rings which facilitate the interaction with metallic surfaces.

II. COMPUTATIONAL DETAILS

In order to elucidate the different inhibition efficiencies and reactive sites of 2,3- Diaminopyridine and 9,10-

Diaminophenanthrene, a computational study of their potential activity as corrosion inhibitors was performed using DFT method at the RHF/STO-6G* level [13]. The inhibition efficiencies of DAP and DAPN were correlated with their molecular electronic parameters. With the aid of Argus Lab (4.0) software, quantum chemical calculations and molecules geometry optimization of these polyamines were carried out by means of the PM3- SCF semi-empirical method [14].

However, DFT has been found to be successful in providing insight into chemical reactivity and selectivity in terms of global parameters. Some global parameters were directly obtained from the output files such as the energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy of the highest occupied molecular orbital [E_{HOMO}] and the dipole moment (μ), while other parameters were derived using appropriate mathematical equations and dependent parameters used by Belghiti *et al*. [15].

III. RESULTS AND DISCUSSION

3.1 Frontier Molecular Orbitals

Table 1 shows the calculated values of the quantum chemical parameters obtained using the Hatrees fock/Density functional theory (HF-DFT) by Hamiltonian Method with PM3 (NDDO) set of Minimal Valence Basis as STO-6G program. The quantum chemical parameters such as E_{HOMO}, E_{LUMO}, dipole moment and E_{LUMO}-E_{HOMO} (ΔE), Ionization energy, absolute electronegativity, global hardness, global softness and global electrophilicity index were obtained. These parameters provide information about the reactive behaviour of molecules. The reactive ability of the inhibitors was considered to be closely related to their frontier molecular orbital (HOMO and LUMO) [16].

The optimized geometries of 2,3-Diaminopyridine and 9,10-Diaminophenanthrene in neutral and protonated forms are shown in figure 1. The usefulness of frontier orbital theory is in prediction the adsorption centres of the inhibitors responsible for the interaction with surface metal.

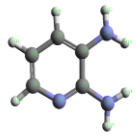
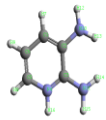
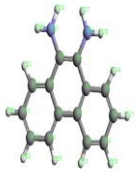
Molecule	Neutral molecule	Protonated molecule
2,3-Diaminopyridine (DAP)		
9,10-Diaminophenanthrene (DAPN)		

Figure 1: The optimized geometries of the DAP and DAPN molecules in neutral and protonated forms in the aqueous phase

In Figures 2 and 3, it is observed that both HOMO and LUMO were distributed mainly around the Benzene rings and Nitrogen atom in the DAP and DAPN molecules. This indicates that both DAP and DAPN are electron rich and are capable of donating electrons to the metal or oxide surface which enhances their tendency to inhibit metal corrosion by forming the inhibitor barrier. The frontier orbitals of a chemical species are very important in defining reactivity [17]. Fukui (1982) first recognized the ease of chemical reaction and the stereoselectivity of the reaction path [17]. A good correlation has been found between the corrosion inhibition efficiency and E_{HOMO} that is often associated with the electron donating ability of the molecule. It is well known that the adsorption of an inhibitor onto a metal surface can occur on the basis of donor-acceptor interaction between the π-electrons of the heterocyclic compound and the vacant d-orbital of the metal surface atoms [18]. A higher value of E_{HOMO} is likely to indicate a higher tendency of the molecule to donate electrons to appropriate acceptors molecules of low empty molecular orbital energy. Increasing value of E_{HOMO} facilitates adsorption and therefore enhances the inhibition efficiency [18]. Conversely, the energy of the lowest unoccupied molecular orbital indicates the ability of the molecules to accept electron. The lower the value of E_{LUMO}, the more probable it is that molecule would accept electrons. Another importance factor considered was the gap between the LUMO and the HOMO energy level of the molecules. Literature reveals those excellent corrosion inhibitors are usually those organic compounds that do not only offer electrons to unoccupied orbital of the metal, but also accept free electron from the metal [19].

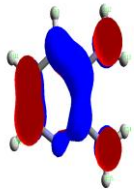
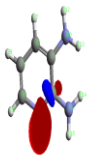
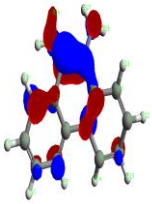
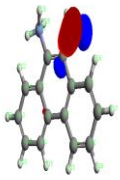
Molecule	Neutral	Protonated
2,3-Diaminopyridine (DAP)		
9,10-Diaminophenanthrene (DAPN)		

Figure 2: The highest occupied molecular orbital (HOMO) density of DAP and DAPN molecules in neutral and protonated forms using DFT at the RHF/STO-6G* basis set level

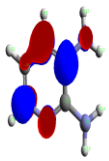
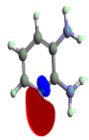
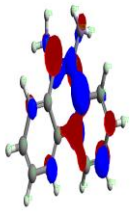
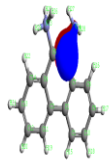
Molecule	Neutral	Protonated
2,3-Diaminopyridine (DAP)		
9,10-Diaminophenanthrene (DAPN)		

Figure 3: The lowest unoccupied molecular orbital density of DAP and DAPN molecules in neutral and protonated forms using DFT at the RHF/STO-6G* basis set level

From table 1, it is observed that the E_{HOMO} value for the DAPN molecule is greater than that of the DAP. The E_{HOMO} values of DAPN and DAP are 0.32eV and -0.0084 eV respectively. This implies that DAPN has the higher tendency of donating electron to the d-orbital of the metal as compared to DAP. On the other hand, it is also observed that the E_{LUMO} for the DAPN is greater than that of the DAP. This indicates that DAP has the lowest tendency of accepting electron from the metal surface as compared to DAPN.

Table 1: Molecular properties of DAP and DAPN molecules in neutral and protonated forms calculated using DFT at the RHF/STO-6G* basis set level in aqueous phase

	E_{HOMO}	E_{LUMO}	ΔE	IE	AE	χ	η	S	ω	ΔE_{b-d}
Neutral										
DAP	-0.0084	0.28	0.29	0.0084	-0.28	-0.14	0.15	6.91	0.034	-0.0036
DAPN	0.32	0.40	0.074	-0.32	-0.40	-0.36	0.037	27.17	0.090	-0.0092
Protonated										
DAP	0.069	0.51	0.44	-0.069	-0.51	-0.29	0.22	4.52	0.073	-0.055
DAPN	0.26	0.90	0.64	-0.26	-0.90	-0.58	0.32	3.10	0.15	-0.081

From table 1, it is observed that the energy gap, ΔE for the DAPN molecule is greater than that of the DAP. The ΔE value for the DAPN and DAP are 0.074 eV and 0.29 eV respectively. This indicates that DAPN molecules with a low energy gap is more polarizable generally associated with a high chemical reactivity, low kinetic stability and is also termed soft molecule. Hence, one could infer that these studied polyamines are more able to interact with metal surface [20].

3.2 Ionization energy and electron affinity

The minimum amount of energy required to remove the most loosely bound electron from the molecules is refer to as ionization energy (IE) [21]. The ionization energies of DAP and DAPN molecules are given in Tables 1. The ionization energy for the DAP and DAPN molecules are as shown below:

$$\mathrm{DAP} + \mathrm{Energy} \rightarrow [\mathrm{DAP}]^{+} + e^{-} \quad (1)$$

$$\mathrm{DAPN} + \mathrm{Energy} \rightarrow [\mathrm{DAPN}]^{+} + e^{-} \quad (2)$$

High ionization energy indicates high stability of molecules, while low ionization energy indicate high reactivity of molecule [22,23].

From table 1, it is observed that the ionization energy for the DAPN is less than that of DAP. The ionization energy (IE) value of DAPN is -0.32eV which has a lower ionization energy compared to DAP with 0.0084eV value of ionization energy. This indicate that DAPN molecule is more reactive on the metal surface and has better inhibition potential than the DAP molecule.

Table 1 shows the result of electron affinities for DAP and DAPN molecules. The electron affinity potential indicates the electronic trend of the molecules and the higher its value, the easier it is to obtain electron from the metal. The electron affinity value for DAP (-0.28eV) is greater than that of the DAPN (-0.40eV). This indicates that DAP molecule having a high electron affinity can easily obtain electron from the metal than DAPN molecule.

3.3. Electronegativity and the electronic chemical potential

Density functional theory (DFT) has been found to be successful in providing insight into chemical reactivity and selectivity, in terms of global molecular properties, such as electronegativity (v) and chemical potential (I) [24]. Thus, for an N-electron system with total electronic energy (E) and an external potential v(r); the chemical potential (I), which is also the negative of the electronegativity (v), has been defined as the first derivative of the E with respect to N at constant v(r) (Eq 3) [25]:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \quad (3)$$

In accordance with the earlier work of Iczkowski and Margrave [26], it should be noted that, when assuming a quadratic relationship between E and N and in a finite difference approximation, Eq. (3) may be written as:

$$\chi = -\mu = -\frac{1}{2}(\mathrm{I}+\mathrm{A}) \quad (4)$$

$$\chi = -\frac{1}{2}(E_{LUMO} + E_{HOMO}) \quad (5)$$

where I and A are the ionization potential and electron affinity, respectively, thereby recovering the electronegativity definition of Mulliken [27].

The ability of molecules to attract electrons to itself is termed electronegativity. The results of electronegativity for DAP and DAPN is as shown in Table 1. The electronegavity value of DAPN molecule is greater than that of the DAP molecule. This implies that DAPN molecule can easily accept electrons and react with metal atom. It is observed that DAPN molecule is more electronegative than DAP, indicating high tendency of attracting electrons.

3.4 Global hardness and softness

The hardness η of an electronic system (Eq 6) is defined as [28]:

$$\eta = \frac{1}{2}\left(\frac{\partial\mu}{\partial N}\right)_{v(r)} = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \quad (6)$$

This is a global quantity, often called ‘‘absolute hardness’’, to emphasize the fact that its value for a molecule in some environment can be different from its value in isolation. The global softness (S) (Eq 7), is the inverse of global hardness [29]:

$$S = \frac{1}{2\eta} = \left(\frac{\partial \mathrm{N}}{\partial\mu}\right)_{v(r)} \quad (7)$$

Following Janak’s theorem, and according to the valence state parabola model, hardness can be approximated in terms of the energies of HOMO and LUMO as shown in Eq 8:

$$\eta = \frac{\mathrm{I}-\mathrm{A}}{2} = -\frac{1}{2}(E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}) \quad (8)$$

The relationship between hardness and the HOMO-LUMO gap is physically evident. Hard molecules have a high HOMO-LUMO gap and soft molecules have a small HOMO-LUMO gap. The most effective inhibitors for metal corrosive inhibition are the soft base inhibitors. From table 1, it could be observed that DAPN, which has the lower energy gap and the higher softness has the higher inhibition efficiency. To confirmed this statement, the quantum chemical parameters (S) was calculated which measures the softness of the molecule and hence, its reactivity. From table 1, it is observed that DAPN has the higher S value of 27.17 eV compared to that of DAP molecule. Table 1 also present the hardness value (g) obtained for neutral species of the inhibitors. It is observed that the hardness of the neutral form of the DAPN molecule is less than that of the DAP, which is the reverse of that obtained for softness. This indicate that the inhibitor with the least value of global hardness which is DAPN (hence with the higher value of global softness) is the best and vice versa. This is because a soft molecule is more reactive toward a metal surface than a hard molecule [30]. Hardness reflect stability and reactivity of molecules. DAP molecule will easily form stable product with ions than DAPN molecule.

3.5 Electrophilicity Index

The global electrophilicity index (x) was introduced by Pearson *et al*. [31] and is given in Eq 9:

$$\omega = \frac{\mu^2}{4\eta} \quad (9)$$

According to the definition, this index measures the propensity of chemical species to accept electrons. The higher the value of x, the higher the capacity of the molecule to accept electrons. Thus, a good nucleophile is characterized by low values of I and x; and, otherwise, a good electrophile is characterized by high values of I and x. Using the parabolic model, it can be shown that global electrophilicity index (x), can also be given by Eq 10:

$$\omega = \frac{(\mathrm{I}+\mathrm{A})^2}{8(\mathrm{I}+\mathrm{A})} \quad (10)$$

Table 1 present the calculated values of the electrophilicity index of DAP and DAPN molecules. The result indicates that DAPN has the higher value of ω (0.09eV) compare to DAP (0.034 eV). This implies that DAPN has higher capacity to accept electrons from the partially filled d-orbital of metal.

3.6 Energy Change For Donation And Back Donation Of Charges

It is also important to consider the situation where a molecule receives a certain amount of charge at some center and then back-donates charge through the same center or through another one. To describe the energy change associated with these two processes, Gomez et al. [32], introduced the second order, simple charge transfer formula. This formula is regarded as a two-parameter expression, in which the donation and back-donation processes are differentiated through the use of the values of the chemical potential for each case, while the hardness is fixed to the value of $\eta = (\mu^+ - \mu^-)$ in both situations, where μ^+ and μ^- are the chemical potentials for the donation and back-donation processes, respectively. Thus, when the molecule receives a certain amount of charge, ΔN^+;

$$\Delta E^+ = \mu^+\Delta N^+ + \frac{1}{2}\eta(\Delta \mathrm{N}^+)^2 \quad (11)$$

whereas when the molecule back-donates a certain amount of charge, ΔN^-, then:

$$\Delta E^{-} = \mu^{-}\Delta N^{-} + \frac{1}{2}\eta(\Delta N^{-})^{2} \qquad (12)$$

If the total energy (ΔE_T) change is approximated by the sum of the contributions of Eqs. (11) and (12), and assuming that the amount of charge back-donation is equal to the amount of charge received,

$\Delta N^{+} = -\Delta N^{-}$, then;

$$\Delta E_T = \Delta E^{+} + \Delta E^{-} = (\mu^{+} - \mu^{-})\Delta N^{+} + \eta\left(\Delta N^{+}\right)^{2} \qquad (13)$$

The most favorable situation corresponds to the case when the total energy change (ΔE_T) becomes a minimum with respect to ΔN^{+}, which implies that $\Delta N^{+} = \frac{-(\mu^{+} - \mu^{-})}{2\eta}$

and that;

$$\Delta E_T = \frac{-(\mu^{+} - \mu^{-})^{2}}{4\eta} = \frac{-\eta}{4} \qquad (14)$$

According to Eq. (14), an electronic back-donation process might occur that governs the interaction between the organic inhibitor and the metal surface. The relation also shows that, if both processes occur, namely charge transfer to the molecule and backdonation from the metal surface, the energy change is directly proportional to the hardness of the molecule.

Table 1 indicates that the hardness values are greater than zero and the energy of back donation ($\Delta E_{b\text{-}d}$) values are smaller than zero. As such, it is energetically favourable to donate electrons from these inhibitors to metallic surface and back donate these electrons. The $\Delta E_{b\text{-}d}$ values of the DAPN molecule is greater than that of the DAP molecule.

3.7 Mulliken population analysis

Mulliken population analysis has become a tool for most rreseachers to use in knowing the adsorption centers of inhibitors [33,34]. Most engineering alloys are passive and their surfaces are protected with passive films including a defective oxide barrier layer and a precipitated, porous outer layer when in contact with aqueous solutions under even mildly oxidizing conditions. Thus, this makes it possible for the inhibitor and the outer surface of the barrier layer to interact rather than the inhibitor and the metal surface. This noticeable fact does not seem to have been broadly documented in inhibitor science. It has been established that the more negatively charged a heteroatom is, the greater is its ability to adsorb onto the metal surface through a donor–acceptor type of interaction Obot et al. [35].

Table 2: Mulliken atomic charges for DAP and DAPN molecules

S/N	DAP		DAPN	
	Atom	Charge	Atom	Charge
1	C	-0.2498	C	-0.0521
2	C	-0.1022	C	-0.0420
3	C	0.0016	C	-0.1719
4	N	-0.1775	C	-0.1888
5	C	-0.1416	C	-0.1858
6	C	-0.2395	C	-0.1938
7	N	-0.0870	H	0.2001
8	N	-0.0694	H	0.1924
9	H	0.2004	H	0.1951
10	H	0.2130	H	0.1956
11	H	0.2012	C	-0.0978
12	H	0.1171	C	-0.0926
13	H	0.1042	C	-0.0182
14	H	0.1016	C	0.0108
15	H	0.1280	C	-0.1360
16			C	-0.1700
17			C	-0.1576
18			C	-0.1634
19			N	-0.0248
20			N	-0.0244
21			H	0.1700
22			H	0.1603
23			H	0.1607
24			H	0.1542
25			H	0.0711
26			H	0.0639
27			H	0.0695
28			H	0.0755

Table 2 shows the calculated mullikan atomic charges for DAP and DAPN molecules calculated using DFT at the RHF/STO-6G* basic level. The result reveals that all the Nitrogen and some carbon atoms carries negative mullikan charge densities indicating possible sites of adsorption on the surface. Moreover, some carbons atoms (C3 of the DAP and C14 of the DAPN) and all the hydrogen atoms carries positive mullikan charge densities. This indicates the sites in which the molecules could accept electron from the un-occupied d-orbital of the metals.

3.8 Molecular Electrostatic Potential (MEP)

The reactive sites of a molecule could be well understood by molecular electrostatic potential [36–38]. In this study, the MEP was calculated at the PM3 optimized geometry. The

MEP shows molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of colour grading, and is very useful in research of molecular structure with its physiochemical property relationship [39,40]. Different values of the electrostatic potential are represented by different colours.

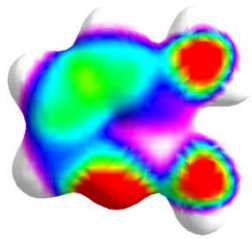
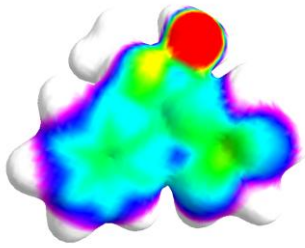
Diaminopyridine derivative	Esp-Mapped Density
2,3-Diaminopyridine (DAP)	
9,10-Diaminophenanthrene (DAPN)	

Figure 4: Molecular electrostatic potential-mapped density of DAP and DAPN molecules

In most of the MEP, the maximum negative region which is the preferred site for electrophile attack indicates as red color, while the maximum positive region indicated by blue colour is the preferred site for nucleophilic attack. Potential increases in the order red < Orange < Yellow < Green < blue. As can be seen from the MEP of the DAP and DAPN (Figure 4), the negative potentials are over the electronegative Nitrogen atom, suggesting the existence of electrostatic farces between these moieties and metal surface.

IV. CONCLUSION

Quantum chemical calculations showed DAP and DAPN molecules adsorbed on the metal surface as molecular species using Nitrogen and cyclic carbons as its active centres. The inhibition ability of DAP and DAPN molecules showed close correlation as it can be deduced from their quantum chemical parameters. From the results, DAPN molecule showed more inhibition potential on metal surface than DAP molecule.

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