

Computational Assessment of the Corrosion Inhibition Potentials of Some Polyamines Using Density Functional Theory

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Abstract: The theoretical studies of corrosion inhibition potentials of three polyamine derivatives {2, 3-diaminophenazine (DAPH); 1, 2-diaminoanthraquinone (DAA) and 2, 3-diaminonaphthalene (DAN)} were investigated using Density Functional Theory with RHF/STO-6G* method. Quantum chemical parameters (such as E_{HOMO} , E_{LUMO} , energy gap, ionization energy, electron affinity, global hardness, global softness, electrophilicity index, back donation, absolute electronegativity) were used to predict the corrosion inhibition potentials. Corrosion inhibition potentials increased with increase in E_{HOMO} , absolute electronegativity, global softness, electrophilicity index and decreasing energy gap, E_{LUMO} , global hardness and back donation. It was observed that the predictive corrosion inhibition potentials decreased as follows: DAPH > DAA > DAN. Also, the sites of likely electrophilic attack were located on atoms (nitrogen and oxygen) as shown by high negative Mulliken charges of these atoms. Molecular electrostatic potentials (MEPs) also provided further insight into the binding sites of these molecules on the metal-surface.

Keywords: Metal, Corrosion, Inhibition, Quantum, polyamine

I. INTRODUCTION

Globally, challenges facing industries right from the inception, is corrosion of metals like Fe, Ni, Al, Cr, Ti and their alloys when exposed to aggressive media [1–3]. National Association of Corrosion Engineers reported that the global corrosion expenditure is about US \$ 2.5 trillion; and proper implementation of measures for prevention of corrosion can save more than \$ 875 billion annually [4]. Hence, this can be successfully accomplished with effective corrosion inhibitors.

Among several measures of corrosion prevention, inhibitors of corrosion have been widely applied in various fields such as, petroleum extraction and refining, iron and steel, electric power, construction and several others due to economy and high efficiency [5–7]. The extent upon which the inhibitor interacts on the surface of metal makes the inhibitor more effective for corrosion prevention [8–10]. In industries, most

effective inhibitors are organic compounds which contain high electronegative heteroatoms such as, sulphur, oxygen, nitrogen through which they are adsorbed on the surface of metal [10,11].

Experimental methods like weight loss, electrochemical potentiodynamic polarization and electrochemical impedance spectroscopy used in evaluating inhibition action of inhibitors are costly, time-consuming, and are often deficient in elucidating inhibition mechanisms. As such, theoretical method has been created to unfold the mechanism of corrosion inhibition [9,12–14]. Quantum chemical methods were introduced by Vosta in 1971 to investigate corrosion inhibition and this founded the field of quantum corrosion electrochemistry [15]. It was mainly used in exploring and establishing connection between inhibition efficiency and molecular structure, but it can now be used in defining how inhibitor molecules and metal surfaces interact [9,16,17]. Exact parameter values are calculated for even hugely complex molecules at low cost using quantum chemical studies [18].

Literature reveals that organic compounds have been successfully explored as potential corrosion inhibitors for metals [19–22]. However, a close examination of some of these organic compounds shows that some of them are not environmentally friendly, while others are expensive. These and many other factors have prompted a continuous search for better corrosion inhibitors. The present study is aimed at correlating the electronic structures of these polyamines {2, 3-diaminophenazine (DAPH); 1, 2-diaminoanthraquinone (DAA) and 2, 3-diaminonaphthalene (DAN)} with their corrosion inhibition potential. The observable effect of inhibition is strengthened by heteroatoms such as Nitrogen and Oxygen, and π bonds in the aromatic rings which facilitate metallic surface interaction. The polyamines chosen for this study are shown in Figure 1.

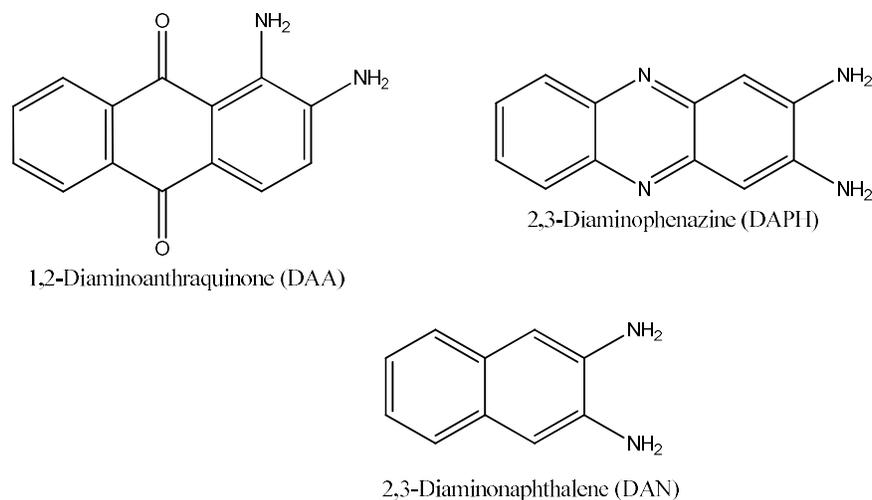


Figure 1: Chemical structures of polyamine molecules

II. QUANTUM CHEMICAL ANALYSIS

Three new polyamines were theoretically studied using DFT method at the RHF/STO-6G* level [23]. The electronic parameters of the polyamines were correlated with inhibition efficiencies. Quantum chemical analysis and molecules geometry optimization of these polyamines in both unprotonated and protonated forms were analysed using PM3-SCF semi-empirical method using Argus Lab (4.0) software. Some global parameters were directly obtained from the output files, while other parameters were derived using appropriate mathematical equations and dependent parameters [24].

According to DFT - Koopman's theorem [25]:

$$\text{Ionization energy (eV), IE} = -E_{HOMO} \quad - \quad (1)$$

$$\text{Electron affinity (eV), AE} = -E_{LUMO} \quad - \quad (2)$$

$$\text{Energy gap (eV), } \Delta E_g = E_{LUMO} - E_{HOMO} \quad - \quad (3)$$

$$\text{Absolute electronegativity (eV), } \chi = \frac{-1}{2}(E_{HOMO} + E_{LUMO}) \quad - \quad (4)$$

$$\text{Global hardness (eV), } \eta = \frac{-1}{2}(E_{HOMO} - E_{LUMO}) \quad - \quad (5)$$

$$\text{Global softness (eV)}^{-1}, S = \frac{-2}{E_{HOMO} - E_{LUMO}} \quad - \quad (6)$$

$$\text{Global electrophilicity index (eV), } \omega = \frac{E_{HOMO} + E_{LUMO}}{8} \quad - \quad (7)$$

$$\text{Back donation (eV), } \Delta E_{b-d} = \frac{E_{HOMO} - E_{LUMO}}{8} \quad - \quad (8)$$

III. RESULTS AND DISCUSSION

3.1 Frontier Molecular Orbitals

The quantum chemical parameters values calculated using the Hartree-fock/ DFT by Hamiltonian method with PM3 (NDDO) set of Minimal Valence Basis as STO-6G program are shown in Tables 1 and 2. The quantum chemical parameters like 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 show the reactive behaviour of molecules. HOMO and LUMO energies are closely related the reactive tendency of the inhibitors [26]. The optimized geometry of polyamine molecules in unprotonated and protonated forms is shown in Figures 3 and 4 respectively. As we know, frontier orbital theory can be used in predicting centres of adsorption of the inhibitor with surface metal atoms.

It could also be easily seen in figure 3 that the HOMO was distributed around the aromatic rings of benzene and Nitrogen atom of the unprotonated molecule, while partially distributed in the protonated form; whereas the LUMO shown from figure 4 was distributed on the entire molecules. It shows clearly the differences in electron distribution of these molecules. The distribution of electron on DAPH molecule is concentrated in multiple π electrons of benzene, and makes it more capable of binding toward metal surfaces compared with DAN and DAA. The distribution of electron on DAN molecule spreads out over the molecule so that it has lower capability towards metal surfaces compared with DAPH and DAA. Frontier orbitals (HOMO and LUMO) are the principal factors governing the ease of chemical reactions and the stereo-selectivity reaction path was first recognized by Fukui [27]. The occurrence of adsorption of inhibitor on metallic

surface is due to donor-acceptor interactions. Moreover, the gap between LUMO and HOMO energies levels of the molecule is a significant factor to be considered. Excellent corrosion inhibitors donate and accept free electrons from metals [28].

The high HOMO energy confirms electron donating ability of the polyamine molecules to unoccupied d - orbital of the metal indicating electrostatic interaction (physisorption) [29]. The low LUMO energy confirms electron accepting tendency from the surface of metal. The smaller the energy gap the more efficient the inhibitor [30].

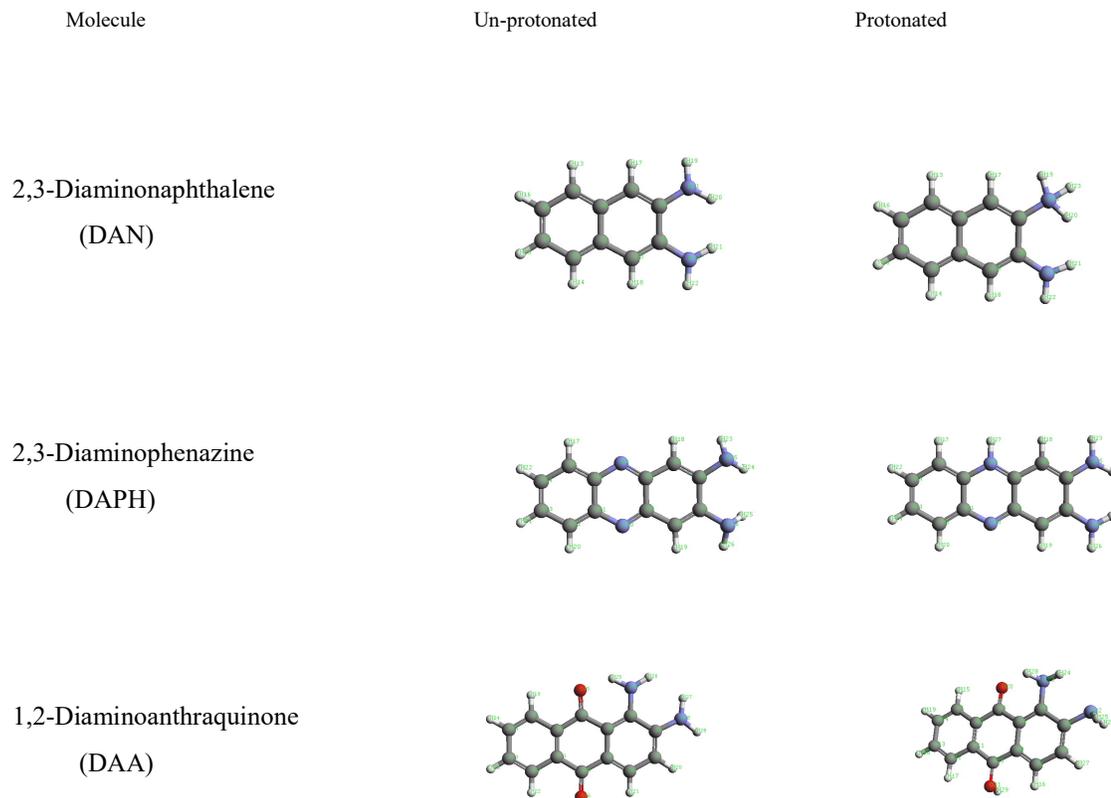
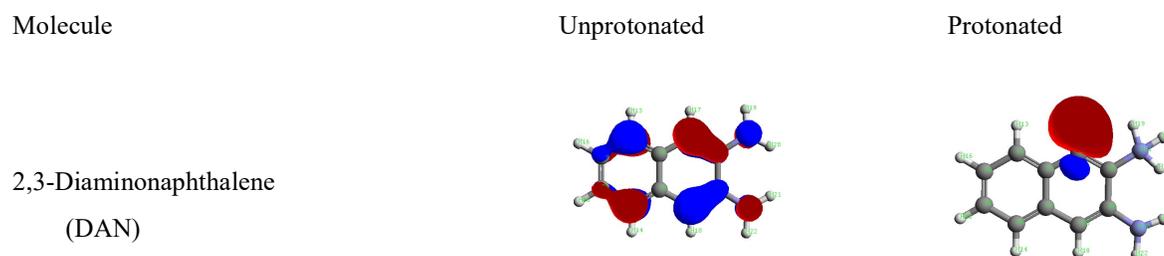
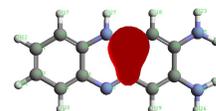
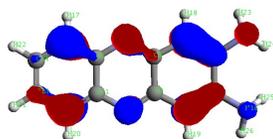


Figure 2: The optimized geometries of the polyamines in their un-protonated and protonated forms in the aqueous phase



2,3-Diaminophenazine
(DAPH)



1,2-Diaminoanthraquinone
(DAA)

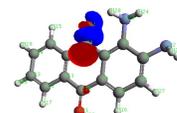
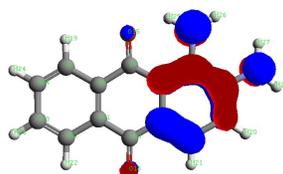


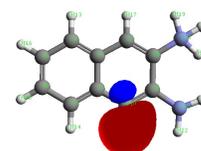
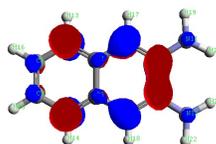
Figure 3: The highest occupied molecular orbital (HOMO) density of DAN, DAPH and DAA molecules using DFT at the RHF/STO-6G* basis set level

Molecule

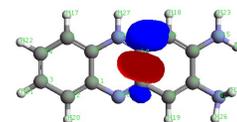
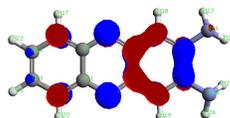
unprotonated

protonated

2,3-Diaminonaphthalene
(DAN)



2,3-Diaminophenazine
(DAPH)



1,2-Diaminoanthraquinone
(DAA)

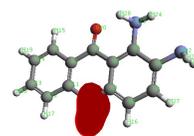
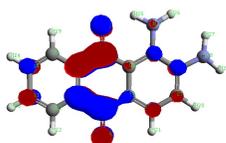


Figure 4: The lowest unoccupied molecular orbital density of DAN, DAPH and DAA molecules using DFT at the RHF/STO-6G* basis set level

Literature reveals that in acid solutions, molecules undergo protonation and can therefore exist as a mixture of unprotonated and protonated molecules [30,31]. These polyamine molecules may adsorb on Fe-surface in

unprotonated or protonated forms. Tables 1 and 2, show the calculated parameters of the unprotonated and protonated molecules respectively. From table 1, it is observed that the E_{HOMO} for the polyamine models in unprotonated form

follows: DAPH > DAA > DAN. The E_{HOMO} value of DAPH is 1.052 eV in unprotonated form which is higher compared to other molecules. It predicts that DAPH has greater tendency of donating electrons to d-orbital of metal as compare to other

studied compounds. From tables 1 and 2, E_{HOMO} and E_{LUMO} values are lower for unprotonated form than protonated form of these polyamines, indicating decrease in electron accepting and electron donating tendencies of the inhibitor molecules.

Table 1: Molecular properties of unprotonated polyamines calculated using DFT at the RHF/STO-6G* basis set level in aqueous phase

	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	μ (debye)	IE (eV)	AE (eV)	χ (eV)	η (eV)	S (eV) ⁻¹	ω (eV)	$\Delta E_{\text{b-d}}$ (eV)
DAN	-0.023	0.79	0.81	5.76	0.023	-0.79	-0.38	0.41	2.46	0.096	-0.102
DAPH	1.052	1.082	0.030	9.50	-1.05	-1.082	-1.067	0.015	66.89	0.27	-0.0037
DAA	0.57	0.77	0.19	2.30	-0.57	-0.77	-0.67	0.097	10.35	0.17	-0.024

From table 1, it is observed that the ΔE for the studied polyamine models in unprotonated form follows: DAPH > DAA > DAN. From table 2, the ΔE of DAA is higher compare to DAN molecules, indicating tendency of not easily donating electrons in protonated form. Hence, one could infer

that these polyamines are more able to interact with metal-surface. Infact, the protonated forms are more attracted (through electrostatic interactions) to metal atoms by already adsorbed anion [32].

Table 2: Molecular properties of protonated polyamines calculated using DFT at the RHF/STO-6G* basis set level in aqueous phase

	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	μ (debye)	IE (eV)	AE (eV)	χ (eV)	η (eV)	S (eV) ⁻¹	ω (eV)	$\Delta E_{\text{b-d}}$ (eV)
DAN	0.58	0.70	0.12	5.94	-0.58	-0.70	-0.64	0.061	16.41	0.16	-0.015
DAPH	1.12	1.15	0.022	9.64	-1.12	-1.15	-1.13	0.011	89.69	0.28	-0.0028
DAA	0.55	0.76	0.21	9.15	-0.55	-0.76	-0.65	0.10	9.59	0.16	-0.026

The donor-acceptor interactions of unprotonated and protonated forms of polyamines may be between π - π electrons in the heterocyclic rings and σ - (non- shared) electron pairs of the heteroatoms to create a chemical linked with d-orbitals of the metal surface.

3.2. Dipole moment

The dipole moment describes the polarity of a molecule. The inhibition efficiencies increase with decreasing dipole moment of inhibitors [33]. The positive sign of the dipole moment, μ indicates that inhibitors adsorbed on the surface of metal by physical mechanism [34]. The results presented in Tables 1 and 2, show that DAPH has high value of dipole moment compare to DAN and DAA molecules, indicating high inhibition efficiency. The increase in dipole moment increases the adsorption strength between the inhibitors and the surface of metal. It is clear from the results that dipole moment, μ values are positive indicating physical adsorption of these polyamine molecules on the metal surfaces.

3.3. Electronegativity and the electronic chemical potential

Sanderson's principle of electronegativity equalization provides a theoretical justification that is, when two or more atoms form a molecule, their electronegativities become adjusted to the same intermediate value [35]. Electronegativity represents the tendency of molecules to attract electrons. The electronegativity of these polyamine molecules follows the trend: DAPH > DAA > DAN. This

implies that DAPH molecule can easily accept electrons and react with metal atoms. From the results, DAPH molecule is more electronegative compare to DAA and DAN molecules indicating high tendency of attracting electrons.

3.4. Global hardness and softness

The correlation between hardness and energy gap is obvious. It is apparent that the higher the stability of a molecule, the larger the energy gap [36]. Therefore, an electronic system with a larger HOMO-LUMO gap is less reactive than one having a smaller gap. This is based on the Maximum Hardness Principle [37]. Tables 1 and 2 show quantum chemical descriptors for DAPH, DAA and DAN molecules in the unprotonated and the protonated forms respectively using DFT with the RHF/STO-6G* basis set in aqueous phase [38]. Hard molecules have a high HOMO-LUMO gap and soft molecules have a small HOMO-LUMO gap. Thus soft base inhibitors are the most effective for metal corrosion inhibition [39]. From Tables 1 and 2, DAPH molecule has the lowest energy gap, indicating high softness and efficiency. This could also be confirmed by calculating the softness of a molecule and hence, its reactivity. From Table 1, the order with which the softness and reactivity increase is: DAN < DAA < DAPH. Table 1 also presents the hardness values, g , obtained for the protonated molecules. It is observed that hardness of protonated molecules follows the order: DAPH < DAA < DAN, the reverse of that obtained for softness. Hardness reflects stability and reactivity of molecules. According to the

principle of “hard close to hard and soft close to soft”, DAN molecule easily forms stable products with ions.

3.5. Electrophilicity index

The electrophilicity index (ω) was introduced by Parr *et al.* [40]:

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

The receiving of electrons by molecules is measured using electrophilicity index. The higher the electrophilicity, the higher the ability of a molecule to receive electrons. Thus, a good nucleophile is characterized by low values of dipole moment and electrophilicity and a good electrophile is characterized by high values of dipole moment and electrophilicity. Using the parabolic model, electrophilicity index (ω) is given by [41]:

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

The electrophilicity index of these polyamines in the unprotonated and the protonated forms is given in tables 1 and 2 respectively, in order to determine which form has the highest propensity to accept electrons from the metal surface. The results presented in Tables 1 and 2 indicate that DAPH has the highest value of ω for both the unprotonated and the protonated forms of these polyamines, inferring that it has the highest capacity to accept electrons from the partially filled d-orbital of metal. The electrophilicity index of these polyamine molecules follow the trend: DAPH > DAA > DAN.

3.6. Energy change for donation and back donation of charges

It is also important to consider the situation where a molecule accepts charges at some centers and then back-donates the charges through the same or different centers. The energy changes associated with these two processes is the second order simple charge transfer formula [42].

If the two processes occur, the energy change is proportional to the hardness of the molecule. As indicated in Tables 1 and 2, the hardness values are greater than zero and the energy of back donation (ΔE_{b-d}) values are smaller than zero in both the unprotonated and the protonated forms. Therefore, it is energetically favourable to give electrons from these inhibitors to the metallic surface and back-donate these electrons. The ΔE_{b-d} values increased in the order i.e., DAPH > DAA > DAN in both unprotonated and protonated forms [29].

Table 3: Mulliken atomic charges for the polyamine molecules

DAN		DAPH		DAA	
Atom	Charge	Atom	Charge	Atom	Charge
1C	-0.1937	1C	-0.1604	1C	-0.1663
2C	-0.0075	2C	-0.0757	2C	-0.0901
3C	-0.0076	3N	-0.0332	3C	0.3588
4C	-0.1937	4C	-0.0020	4C	-0.1105
5C	-0.1952	5C	-0.2433	5C	-0.0135
6C	-0.1952	6C	-0.0725	6C	-0.1315
7C	-0.2804	7C	-0.1016	7C	-0.2272
8C	-0.0209	8C	-0.2097	8C	-0.1120
9C	-0.0209	9C	-0.0126	9C	-0.1442
10C	-0.2803	10N	-0.0329	10C	0.3773
11N	-0.1274	11C	-0.0748	11C	-0.1129
12N	-0.1274	12C	-0.1498	12C	-0.1605
13H	0.1931	13C	-0.1861	13C	-0.1886
14H	0.1931	14C	-0.1839	14C	-0.1826
15H	0.1893	15N	0.0048	15H	0.2276
16H	0.1893	16N	0.0058	16H	0.2304
17H	0.2009	17H	0.2134	17H	0.2251
18H	0.2010	18H	0.2230	18H	0.2012
19H	0.1269	19H	0.2224	19H	0.2009
20H	0.1149	20H	0.2111	20O	-0.2918
21H	0.1148	21H	0.2030	21O	-0.3413
22H	0.1269	22H	0.2006	22N	-0.0421
		23H	0.0696	23N	-0.0145
		24H	0.0632	24H	0.0706
		25H	0.0543	25H	0.0846
		26H	0.0673	26H	0.0744
				27H	0.0753
				28H	0.2033

3.7. Mulliken population analysis

The Mulliken charges distribution of the polyamine molecules obtained with DFT at the RHF/STO-6G* level is presented in Table 3. The more negative the atomic charges of the adsorbed centre are, the easier the atom donate electron to unoccupied d-orbital of metal [9,43]. It is obvious from Table 3 that all the heteroatoms (Nitrogens and Oxygens) present in these molecules have high negative mulliken charge densities indicating possible sites of adsorption on the surface of metal. However, negative charge densities occur also on the carbon atoms of these compounds, which also indicate good adsorption sites. The other atoms with excess negative charges subsidize towards the electron donation or electron delocalization in adsorption of organic molecule on the surface of metal [44].

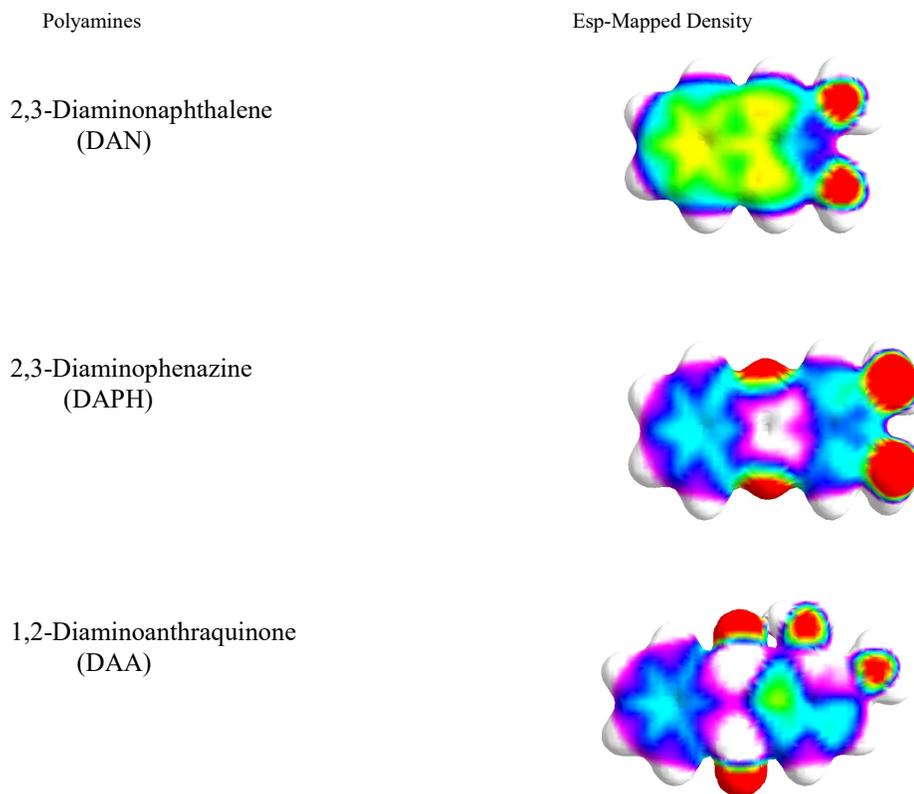


Figure 5: Molecular electrostatic potential-mapped density of DAN, DAPH and DAA molecules

3.8. Molecular Electrostatic Potential (MEP)

MEP is a descriptor in understanding the reactive sites of a molecule [45]. In the present study, the MEP was carried out using the PM3 optimized geometry [9]. The MEP displays positive, negative and neutral electrostatic potential regions using colour grading [46]. In MEP, the maximum negative region is indicated as red colour, and is the preferred site for electrophile attack, while the maximum positive region indicated as blue colour is the preferred site for nucleophilic attack. Electrostatic potential increases in the order: red < Orange < Yellow < Green < blue. The positive potentials are over the cyclic carbon atoms indicating preferred site for nucleophilic attack. For these three polyamines, the deep red colour is at the regions containing heteroatoms (Nitrogen and Oxygen atoms), suggesting the existence of electrostatic forces. Chemical forces also exist on other parts of the molecules (Nucleophilic reactivity) [47].

IV. CONCLUSION

The adsorption of these molecules on the metal surface can occur on the basis of donor-acceptor interactions between the lone pairs on heteroatoms or π electrons of the molecule and the empty d-orbital of the metal atom. DAPH, DAA and DAN molecules possess corrosion inhibition potentials as can be deduced from their quantum chemical parameters. DAPH

molecule showed high corrosion inhibition potential on metal compare to DAA and DAN.

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