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Semi-Empirical Quantum Chemical Studies of 4-(benzylideneamino)phenylpyrazol-3-one Derivatives as Corrosion Inhibitors for Mild Steel

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Abstract

Quantum chemical study was used to investigate the corrosion inhibition performance of three inhibitors namely: 4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one(BMPP),4-(benzylideneamino)-1-methyl-5-nitro-2-phenyl-1,2-dihydro-3H-pyrazol-3-one(BNPP) and 4-(benzylideneamino)-2-methyl-5-oxo-1-phenyl-2,5-dihydro-1H-pyrazole-3-sulfinic acid(BOPS) on carbon steel using Restricted Hartree-fock level (RHF) Parameterized Model 3 (PM3) semi-empirical Self Consistent Field Molecular Orbital method. The calculated quantum chemical parameters studied were E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap (ΔE), hardness (η), softness (S), the absolute electronegativity (χ), the electrophilicity index (ω), the total energy(E_{tot}) and the fractions of electrons transferred (ΔN). The Mulliken atomic charges were applied to the estimation of adsorption centers of inhibitors. The sites of adsorption activity were estimated from the net charges on the molecules. The relationship between the inhibitory efficiency and quantum chemical parameters has been discussed in order to elucidate the inhibition mechanism. Comparative studies on the inhibition efficiency of the 4-(benzylideneamino)phenylpyrazol-3-one derivatives showed that they could be ranked as follows BOPS > BNPP > BMPP.

Keywords

Corrosion, Inhibition, Quantum, 4-(benzylidene amino)phenylpyrazol-3-one

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1. Introduction

Corrosion is a global problem in the developing and developed countries. The protection of metals against corrosion is an important issue. Numerous remediation techniques have been suggested and implemented to protect metals against corrosion. Among these remediation techniques is the use of corrosion inhibitors. Corrosion inhibitors block the corrosive material (solution) from coming into contact with metal through either physisorption or chemisorption. It has been reported that aromatic or long chain heterocyclic compounds containing nitrogen, oxygen and sulphur are effective inhibitors [1]. Several researchers [2-5] have applied semi-empirical quantum chemical studies in elucidating the mechanism of corrosion inhibition of heterocyclic organic compounds. Quantum chemical studies on corrosion inhibition enable us to determine the mechanism by which inhibitors retard corrosion. The reactivity of a molecule is a function of its electronic properties such as the electron density, the dipole moment, partial Mulliken charges, highest occupied molecular orbital, lowest unoccupied molecular orbital, energy gap and total energy. Molecules possessing high density are good corrosion inhibitors because they are able to donate electrons to the partially filled vacant d orbital of the metal forming coordinate covalent bond. The order of inhibition

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efficiency preference for heteroatom's is as follows O < N < S < P [6]. The most electronegative atom has the least tendency to donate electrons. The main objective of this corrosion inhibitor computationalresearch is to gain insight into the mechanisms by which 4-(benzylideneamino)phenylpyrazol-3-one inhibitors inhibit corrosion. Indeed, the effectiveness of the overall process is a function of the metal surface, corrosive media, molecular and electronic structure, and concentration of the inhibitor, as well as temperature and other environmental considerations [28-32]. Several organic compounds have been studied by computational simulations but theoretical reports on 4-(benzylideneamino)phenylpyrazol-3-one are rather scarce. In this present study, we are reporting theoretical study on electronic and molecular structures of: 4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one(BMPP),4-(benzylideneamino)-1-methyl-5-nitro-2-phenyl-1,2-dihydro-3H-pyrazol-3-one(BNPP) and 4-(benzylideneamino)-2-methyl-5-oxo-1-phenyl-2,5-dihydro-1H-pyrazole-3-sulfinic acid(BOPS) and to determine relationship between molecular structure of the compounds and inhibition efficiency on mild steel from gas phase. This was done by discussing the quantum chemical and structural parameters.

2. Methodology

2.1. Structure of Organic Molecules

The structures of organic molecules 4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (BMPP), 4-(benzylideneamino)-1-methyl-5-nitro-2-phenyl-1,2-dihydro-3H-pyrazol-3-one(BNPP) and 4-(benzylidene amino)-2-methyl-5-oxo-1-phenyl-2,5-dihydro-1H-pyrazole-3-sulfinicacid(BOPS) were drawn using ACDlab ChemSketch 11.0 software. The structures were saved as Mol file and taken as input for the quantum chemical studies.

2.2. Quantum Chemical Calculations

Theoretical calculations (total energy, electronic energy, ionization potential, E_{HOMO} and E_{LUMO} were carried out at the Restricted Hartree-fock level(RHF) using Parameterized Model 3(PM3) semi-empirical Self Consistent Field Molecular Orbital method in the MOPAC 2009 (Version: 9.258L) implemented on an Pentium(R) Dual core CPU 2.30GHz [7]. Optimized structures for the HOMO and LUMO energy were performed using Arguslab 4.01 software [8]. Electron affinity for the inhibitors ware calculated from E_{LUMO} (EV) as shown in equation 1[9].

$$EA = -E_{LUMO} \quad (1)$$

Equation 2 and 3 were used in the evaluation of electronegativity (χ) and the chemical hardness (η) [10]

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

$$\eta = \frac{IP-EA}{2} \quad (3)$$

Chemical softness (σ) can also be called electron polarizability. It was calculated according to the expression in equation 4 [10]. It estimates the amount of electron received by atoms or group of atoms.

$$\sigma = \frac{1}{\eta} \quad (4)$$

When iron and inhibitor are in contact, the higher electronegative specie (iron) will attract electrons to itself until there is a balance in chemical potential. Therefore the fraction of electrons transferred (ΔN) from the inhibitor molecule to the metallic atom was calculated according to Pearson electronegativity scale [11] have been used to calculate the fraction of electrons transferred (ΔN) from the inhibitor molecule to iron.

$$\Delta N = \frac{\chi_{iron}-\chi_{inhibitor}}{[2(\eta_{iron}+\eta_{inhibitor})]} \quad (5)$$

Where χ_{iron} and $\chi_{inhibitor}$ represent the absolute electronegativity of iron and inhibitor molecule respectively.η_{iron} and $\eta_{inhibitor}$ represent the absolute hardness of iron and the inhibitor molecule respectively. Theoretical value of χ_{iron} and η_{iron} were taken to be7.0 eV/mol and0 eV/mol.

Electrophilicity index (ω) is the estimation of the electrophilic power of a molecule [12].

$$\omega = \frac{\chi^2}{2\eta} \quad (6)$$

The greater the valueof ω, the more the ability of the molecule to accept electrons.

3. Results

The structure of the inhibitors 4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (BMPP), 4-(benzylideneamino)-1-methyl-5-nitro-2-phenyl-1,2dihydro-3*H*-pyrazol-3-one(BNPP) and 4-(benzylideneamino)-2-methyl-5-oxo-1-phenyl-2,5-dihydro-1*H*-pyrazole-3-sulfinic acid (BOPS) are shown in Figures 1 – 3. The Quantum chemical descriptors for the inhibitors are presented in Table 1. Mulliken atomic charges are shown in Tables 2 – 4. The optimized structures for the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals of the inhibitors BMPP, BNPP and BOPS are shown in Figures 4 – 9 respectively.

Table 1. Quantum chemical parameters for the inhibitors.

S/N	Quantum chemical parameters	BMPP	BNPP	BOPS
1	Total energy (TE) (eV)	-2867.21	-3499.09	-3522.90
2	Electronic energy (EE)(eV)	-18510.88	-23328.58	-23675.80
3	Ionization potential (IP) (eV)	9.19	8.88	8.67
4	E_{HOMO} (EV)	-8.72	-8.88	-8.46
5	E_{LUMO} (EV)	-3.46	-4.20	-3.05
6	ΔE (EV)	-5.26	- 4.68	-5.41
7	Electron affinity (EA), (eV)	3.46	4.20	3.05
8	Electronegativity (χ)	6.33	6.54	5.86
9	Chemical hardness (η)	2.87	2.34	2.81
10	Chemical softness (σ)	0.35	0.43	0.36
11	Fraction of electrons transferred (ΔN)	0.12	0.98	0.20
12	Electrophilicity index (ω)	57.24	49.73	47.69

Table 2. Mulliken Atomic Charges for 4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (BMPP).

Atoms	Charges
1 C	-0.0606
2 C	-0.0521
3 C	0.0193
4 C	-0.0767
5 C	-0.2312
6 C	-0.0662
7 N	0.0659
8 N	0.2966
9 C	0.2043
10 C	-0.6370
11 C	-0.0493
12 N	-0.0080
13 C	0.0989
14 C	0.4075
15 C	0.1069
16 C	-0.1195
17 C	-0.0524
18 C	-0.1027
19 C	-0.2304
20 C	-0.1935
21 C	-0.0451
22 O	-0.2747

Table 3. Mulliken Atomic Charges for 4-(benzylideneamino)-1-methyl-5-nitro-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (BNPP).

Atom Numbers	Charges
1C	-0.0697
2C	-0.0312
3C	0.1130
4C	-0.0025
5C	-0.1714
6C	-0.0576
7N	-0.1906
8N	-0.2367
9C	0.3149
10C	-0.0830
11C	0.2852
12N	-0.2842
13C	0.5348
14C	0.5842
15C	-0.0335
16C	-0.0545
17C	-0.0693
18C	-0.1058
19C	-0.0766
20C	0.0710
21O	-0.2218
22N	0.4216
23O	-0.3210
24O	-0.3153

Table 4. Mulliken Atomic Charges for 4-(benzylideneamino) -2-methyl- 5-oxo-1-phenyl-2,5-dihydro-1*H*-pyrazole-3-sulfinic acid (BOPS).

Atom	Charges
1C	-0.0498
2C	-0.0881
3C	0.1444
4C	-0.0528
5C	-0.1996
6C	-0.1111
7N	-0.2397
8N	-0.1088
9C	0.3258
10C	-1.7594
11C	0.2027
12N	-0.4082
13C	0.3208
14C	0.3974
15C	-0.2327
16C	-0.0418
17C	-0.0493
18C	-0.2703
19C	-0.2460
20C	-0.0147
21O	-0.2398
22S	3.6128
23O	-1.0022
24O	-0.8898

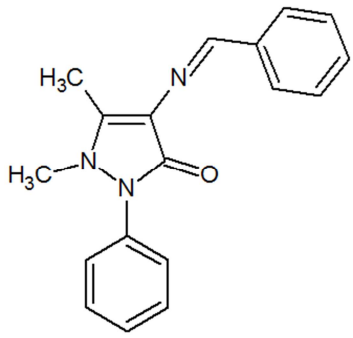

Figure 1. 4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazole-3-one(BNPP).

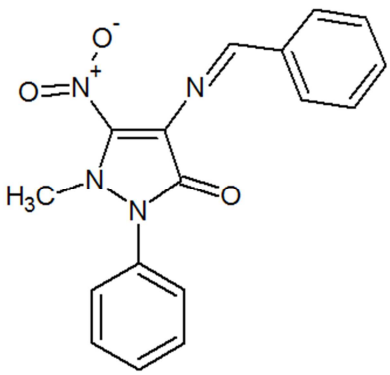

Figure 2. 4-(benzylideneamino)-1-methyl-5-nitro-2-phenyl-1,2-dihdro-3*H*-pyrazole-3-one(BNPP).

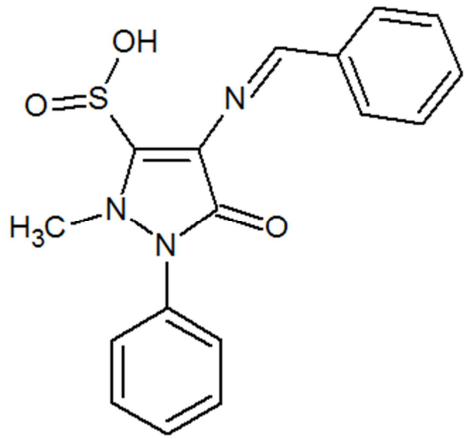

Figure 3. 4-(benzylideneamino)-2-methyl-5-oxo-1-phenyl-2,5-dihdro-1*H*-pyrazole-3-sulfinic acid (BOPS)

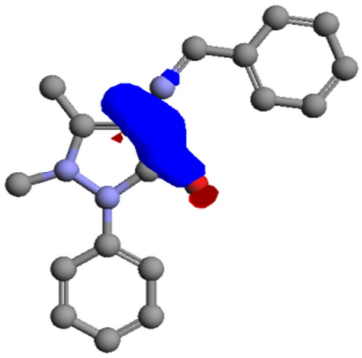

Figure 4. HOMO of 4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (BMPP).

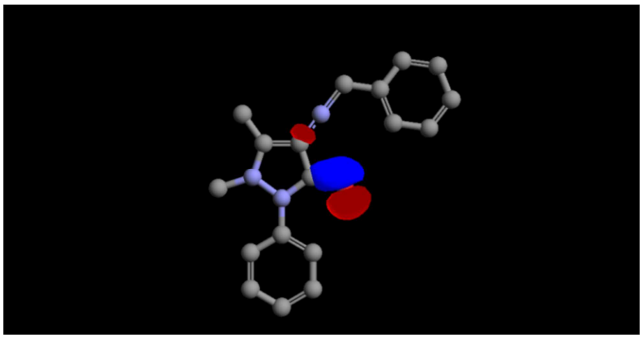

Figure 5. LUMO of4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (BMPP).

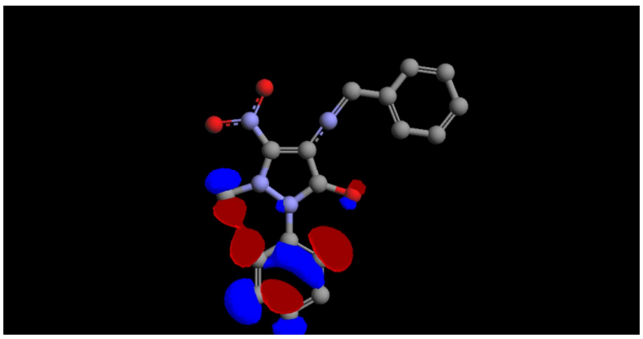

Figure 6. HOMO for 4-(benzylideneamino)-1-methyl-5-nitro-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (BNPP).

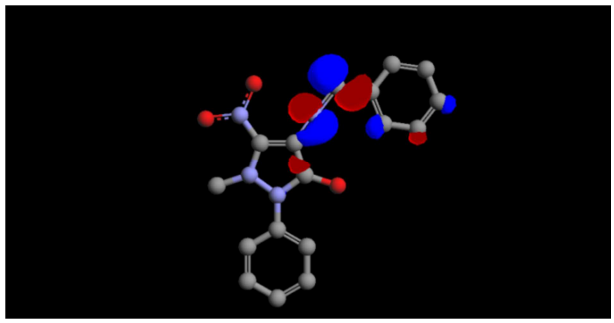

Figure 7. LUMO of 4-(benzylideneamino)-1-methyl-5-nitro-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (BNPP).

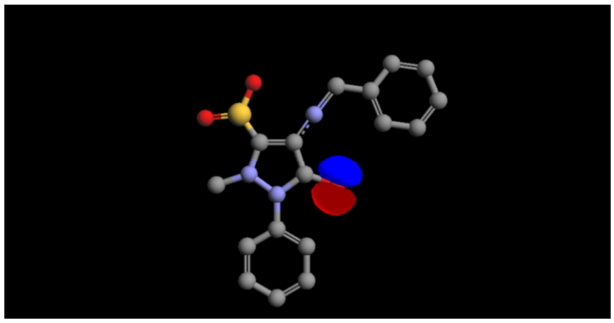

Figure 8. HOMO of4-(benzylideneamino) -2-methyl- 5-oxo-1-phenyl-2,5-dihydro-1*H*-pyrazole-3-sulfinic acid (BOPS).

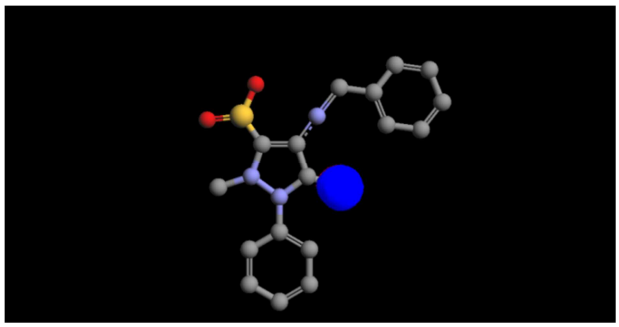

Figure 9. LUMO of4-(benzylideneamino) -2-methyl- 5-oxo-1-phenyl-2,5-dihydro-1*H*-pyrazole-3-sulfinic acid (BOPS).

4. Discussions

Quantum chemical parameters can be used to interprete inhibition efficiency in corrosion studies. Frontier Molecular Orbital theory (FMO) shows that chemical reactivity is a function of interaction between HOMO and LUMO levels of the reacting species [13]. The energy of HOMO values suggests the ability of the molecule to donate electrons to an acceptor with empty low lying orbitals. LUMO energy values suggest the ability of the molecule to accept electrons [14, 15]. The higher is the value of E_{HOMO} of the inhibitor, the greater is its ease of donating electrons to the empty low-lying d-orbital of metal surface and the greater is its inhibition efficiency. BOPS inhibitor showed the highest E_{HOMO} value of -8.46 eV. Based on this assessment it can be deduced that BOPS will offer the highest inhibitory efficiency.

The energy gap, (ΔE = EHOMO − ELUMO) is an important parameter in quantum corrosion studies. Increase in the inhibition efficiency of the molecule is related to decrease in ΔE because the reactivity of the molecule increases [16]. Lesser values of the energy gap suggest good inhibition efficiency, because the energy to remove the valence electron will be low [17]. A soft molecule has low energy gap which makes it more polarizable and is generally associated with high chemical activity and low kinetic stability [18]. Hard molecule is less reactive than a soft molecule because a hard molecule has large energy gap. The results as indicated in Table 1 shows that inhibitor BOPS has the lowest energy gap (-5.41 eV, this means that inhibitor BOPS could have better performance as corrosion inhibitor.

Ionization potential is the energy required to remove an electron from a molecule. The higher the ionization potential the more difficult it is to remove an electron from a molecule. High Ionization energy indicates that the atoms and molecules are stable andinert high while small Ionization energy suggests that the atoms and molecules are highly reactive [19]. The ionization energy values of the inhibitors BMPP, BNPP and BOPS are 9.19, 8.88 and 8.67 eV respectively. BOPS have the lowest ionization energy. This implies that it may have the highest inhibition efficiency.

Chemical hardness signifies the resistance of the electron cloud of the atoms, ions or molecules against deformation or polarization under small perturbation of chemical reaction. A molecule with high chemical hardness has the least tendency to react while a molecule with high chemical softness has high tendency to react. High chemical hardness implies that the molecule has a large energy gap while chemical soft molecule has asmall energy gap. The chemical hardness of the inhibitors BMPP, BNPP and BOPS are as follows 2.87, 2.34 and 2.81. Their chemical softness is 0.35, 0.43 and 0.36 respectively. BNPP has the lowest chemical hardness and highest chemical softness.

Electrophilicity determines the elecrophilic nature of the molecule. The higher the electrophilic, the more tendencythe molecule willact as an electrophile while a low value ofelectrophilicity implies that the molecule mayact as a nucleophile. Table 1 shows the electrophilicity index (ω) for BMPP, BNPP and BOPS inhibitors. BMPP with the highest electrophilicity index (ω) (57.24).

The fraction of electrons transferred (ΔN) informs us on the ability of the molecule to donate electrons and bind to the surface of metals. The greater the value of ΔN, the greater the inhibition efficiency since more electrons will be donated to the surface of the metal. BNPP transferred 0.98 fractions of electrons. Based on fraction of electrons transferred, BNPP will have the highest inhibition efficiency.

Mulliken atomic charges have been applied to the estimation of adsorption centers of inhibitors. It shows the charge distribution over the whole skeleton of the molecule [20] – [27]. It has been reported [20] that the more negatively charged heteroatoms have more tendency to be adsorbed on the metal surface. The calculated Mulliken atomic charges of the inhibitors (Table 2 - 4) shows numerousactive centers. The site ofadsorptionactivity could be estimated from the net charges on a molecule. In BMPP inhibitor, the highest electronegative charge was located on C10 (-0.6370). The highest electronegative charge for BNPP inhibitor was located at O24 (-0.3153). BOPS inhibitor showed its highest electronegativity at C10 (-1.7594).). From the above discussions, it is pertinent to state that BOPS may possess the highest inhibitory efficiency

5. Conclusion

Through Semi-empirical quantum calculations, a correlation between quantum chemical parameters, electronic and molecular structures have been related. The ability of these molecules to inhibit the corrosion process could beestablished. Comparative study of the inhibitors suggest that 4-(benzylideneamino)-2-methyl-5-oxo-1-phenyl-2,5-dihydro-1*H*-pyrazole-3-sulfinic acid (BOPS) has the highest inhibition efficiency because it had the highest HOMO energy and Mulliken atomic charges. It also possessed the lowest energy band gap and ionization potential. Based on the quantum chemical parameters, the inhibition efficiency could be ranked as follows BOPS > BNPP > BMPP.

References

[1] Udhayakala, P., Jayanthi, A and Rajendiran, T. V (2011). Adsorption and Quantum Chemical Studies on the Inhibition Potentials of Some Formazan Derivatives". *Der Pharma Chemica*, 3: 528-539.

[2] Obi-Egbedi, N. O., Obot, I. B., El-Khaiary, M. I., Umoren, S. A. and Ebenso, E. E. (2011) Computational Simulation and Statistical Analysis on the Relationship Between Corrosion Inhibition Efficiency and Molecular Structure of Some Phenanthroline Derivatives on Mild Steel Surface. *International Journal of Electrochemistry*, 6: 5649-5652.

[3] Bereket, G., Ogretir, C., and Yurt, A. (2001). Quantum Mechanical Calculations on Some 4-Methyl-5-Substituted Imidazole Derivatives as Acidic Corrosion Inhibitor for Zinc". *Journal of Molecular Structure* (*THEOCHEM*), 571: 139-145.

[4] Awad, M. K. (2004). Semiempirical Investigation of the Inhibition Efficiency of Thiourea Derivatives as Corrosion Inhibitors". *Journal of Electroanalytical Chemistry*, 567: 219-225.

[5] Udhayakala, P. (2015). Quantum chemical studies on the inhibition potentials of thiophenederivatives for the corrosion inhibitors of carbon steel, Journal of Chemical and Pharmaceutical Research, 7(1): 803-810.

[6] Thomas, J. G. N. (1981) in: Proceedings of the Fifth European Symposium on Corrosion Inhibitors, Ann. Univ. Ferrara., Italy, 453.

[7] Stewart, J. J. P. (1989) "Optimization of parameters for semi-empirical methods"J. Comp. Chem. 10: 209.

[8] Thompson, M. (2004) Argus Lab 4.0.1, Planaria software LLC.

[9] Koopmans, T. (1933). Uber die Zuordnung von Wellenfunktionen und Eigenwertenzu den einzelnen elektroneneines atoms", *Physica,* 1: 104-113.

[10] Parr. R. G. and Pearson, R. G. (1983). Absolute hardness: companion parameter to absolute electronegativity" *J. Ame. Che. Soc*., 105: 7512-7516.

[11] Pearson, R, G.(1988). Absolute electronegativity and hardness: application to inorganic chemistry", *Inorg. Chem.*, 27(4): 734-740.

[12] Islam, NandGhosh, D. C (2012). On the electrophilic character of molecules through its relation with electronegativity and chemical hardness", Int. J. Mol. Sci. 13(2): 2160-2175.

[13] Gece, G.(2008). The Use of Quantum Chemical Methods in Corrosion Inhibitor Studies", *Corrosion Science*, 50: 2981-2992.

[14] Zhang, D. Q., Gao, L. W. and Zhou, G. D. (2004). Inhibition of Copper Corrosion in Aerated Hydrochloric Acid Solution by Heterocyclic Compounds Containing a Mercapto Group," *Corrosion Science*, 46: 3031-3040.

[15] Rahman, H. H. A., Moustafa, A. H. E. and. Awad, M. K. (2012). Potentiodynamic and Quantum Studies of Some AminoAcids as Corrosion Inhibitors for Copper". *International Journal of Electrochemical Science*, **7**: 1266-1287.

[16] Awad, M. K., Mustafa M. R. and Elnga, M. M. A. (2010). Computational Simulation of the Molecular Structure of Some Triazoles as Inhibitors for the Corrosion of metal Surface. *Journal of Molecular Structure*: *THEOCHEM*, 959: 66-74.

[17] Obot, I. B., Obi-Egbedi, N. O. and Umoren, S. A. (2009) "Adsorption Characteristics and Corrosion Inhibitive Properties of Clotrimazole for Aluminium Corrosion in Hydrochloric Acid", *International Journal of Electrochemical Science*, 4: 863-877.

[18] Fleming, I. (1976). Frontier Orbitals and Organic Chemical Reactions", John Wiley and Sons, New York.

[19] Ebenso, E. E., Isabiye, D. A. and Eddy, N. O. (2010). Adsorption and Quantum Chemical Studies on the Inhibition Potentials of Some Thiosemicarbazide for the Corrosion of Mild Steel in Acidic Medium. *International Journal of MolecularSciences*, 11: 2473-2498.

[20] Pearson, R. G. (1986). Absolute Electronegativity and Hardness Correlated with Molecular Orbital Theory. *Proceedings of the National Academy of Sciences of the United States of America*, 83: 8440-8441.

[21] Kabanda, M. M., Shukla, S. K., Singh, A. K., Murulana, L. C. and Ebenso, E. E. (2012) Electrochemical and Quantum Chemical Studies on Calmagite and Fast Sulphone Black F Dyes as Corrosion Inhibition for Mild Steel in Hydrochloric Medium. *International Journal of Electrochemical Science*, 7: 8813-8831.

[22] Gómez, B., Likha, N. V., Domínguz-Aguilar, M. A., Martínez-Palou, R., Vela, A. and Gásquez, J. (2006). Quantum Chemical Study of the Inhibitive Properties of 2-Pyridyl-Azoles", *The Journal of Physical Chemistry B*, 110, 2006: 8928-8934.

[23] Hasanov, R., Sadikoğlu, M. and Bilgiç, S. (2007), Electrochemical and Quantum Chemical Studies of Some Schiff Bases on the Corrosion of Steel in H_2SO_4. *Applied Surface Science*, 253: 3913-3921.

[24] Allam, N. K. (2007). Thermodynamic and Quantum Chemistry Characterization of the Adsorption of Triazole of Trizole Derivatives during Muntz Corrosion in Acidic and Neutral Solutions. *Applied Surface Science*, 253: 4570-4577.

[25] Özcan, M., Dehri, I and Erbil, M. (2004) Organic Sulphur-Containing Compounds as Corrosion Inhibitors for Mild Steel in Acidic Media: Correlation between Inhibition Efficiency and Chemical Structure. *Applied Surface Science*, 236: 155-164.

[26] Roque, J. M., Pandiyan, T., Cruz, J. and García-Ochoa, E. (2008). "DFT and Electrochemical Studies of Tris(benzimidazole-2-ylmethyl)amine as an Efficient Corrosion Inhibitor for Carbone Steel Surface", *Corrosion Science*, 50: 614-624.

[27] Kandemirli, F andSagdinc, S (2007). Theoretical Study of Corrosion Inhibition of Amides and Thiosemicarbazones. *Corrosion Science*, 49: 2118-2130.

[28] Gece, G., Bilgic, S andTurksen, O (2010). Quantum chemical studies of some amino acids on the corrosion of cobalt in sulfuric acid solution, *Materials and Corrosion*, 61(2): 141–146.

[29] Amin, M. A., Khaled, K. F., Mohsen, O. and Arida, H. A (2010). A study of the inhibition of iron corrosion in HCl solutions by some amino acids, *Corrosion Science*, 52: 1684–1695.

[30] Oguzie, E. E. Li, Y. Wang, S. G andWanga, F. (2011), Understanding corrosion inhibition mechanisms - experimental and theoretical approach," *RSC Advances*, 1: 866–873.

[31] Oguike, R. S., Kolo, A. M., Shibdawa, A. M. and Gyenna H. A. (2013). Density functional theory of mild steel corrosion in acidic media using dyes as inhibitor: adsorption onto fe(110) from gas phase, *Physical Chemistry*, 2013: 1–9.

[32] Kalaiselvi, K., Brindha, T., Mallika, J. (2014). Quantum chemical studies on the corrosioninhibition of mild steel by piperidin-4-one derivatives in 1 M H_3PO_4. Open Journal of metal, 4: 73–85.