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A theoretical evaluation on benzothiazole derivatives as corrosion inhibitors on mild Steel

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ABSTRACT

Density functional theory (DFT), using the B3LYP functional was used to study the inhibition performance of two benzothiazole derivatives namely 1,3-benzothiazole-2-amine (BTA) and 6-methyl-1,3-benzothiazole-2-amine (MBTA) which were recently used as corrosion inhibitors for Mild Steel Corrosion in 1 N HCl. The quantum chemical properties such as E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap (ΔE), dipole moment (μ), hardness (η), softness (σ), the absolute electronegativity (χ), the fractions of electrons transferred (ΔN) and the electrophilicity index (ω) were calculated. The local reactivity has been analyzed through the Fukui function and local softness indices in order to compare the possible sites for nucleophilic and electrophilic attacks. The theoretical results are in well accordance with the experimental outcomes.

Keywords: benzothiazole, corrosion inhibitors, DFT, Fukui function, electrophilicity index.

INTRODUCTION

Corrosion is the deterioration of materials by chemical interaction with their environment. In view of the problems created by mild steel corrosion, several research methods on inhibition of its corrosion have been reported and it has been established that the use of inhibitors is one of the best methods for the prevention of the corrosion of mild steel in acidic medium [1]. Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media [2]. Organic compounds, which can donate electrons to unoccupied d orbital of the metal surface to form coordinate covalent bonds, and can also accept free electrons from the metal surface by using their anti-bonding orbital to form feedback bonds, constitute excellent corrosion inhibitors [3]. A number of heterocyclic compounds containing nitrogen, oxygen, and sulfur either in the aromatic or long chain carbon system have been reported to be effective inhibitors [4,5].

Quantum chemical methods are often utilized to elucidate the physicochemical properties of compounds of interest in order to understand their interaction mechanism with the metal surface and to elucidate the centres in the compounds on which such interactions are likely to occur [6]. Density functional theory (DFT) [7] has provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes [8].

Benzothiazole derivatives have been studied extensively for their diverse chemical reactivity and potential broad spectrum of biological activity. They are heterocyclic compounds, widely found in bioorganic and medicinal chemistry with application in drug discovery. Benzothiazole moieties are part of compounds showing numerous biological activities such as antimicrobial [9,10] anticancer [11,12], anti-diabetic [13] activities. They are also antihypertension [14], anti-inflammatory [15], antioxidant [16] and anti HIV [17]. Ru Sun *et al.*, have studied the Raman spectroscopic and density functional theory studies on a benzothiazole-2-thione derivative [18]. Molecular modeling and spectroscopic studies of benzothiazole [19] have been carried out by Sathyanarayanmoorthi *et al.*, A QSAR study and molecular design of benzothiazole derivatives as potent anticancer agents have been carried out by Chen Jincan *et al.*, [20]. Quantum chemical calculations on some substituted benzothiazole derivatives as corrosion inhibitors for brass in acidic media have been investigated by Mohamed *et al.*, [21].

The aim of the present work is to extend the experimental observation of Patel *et al.*, [22], to present a theoretical study of the electronic and structural parameters of 1,3-benzothiazole-2-amine (BTA) and 6-methyl-1,3-benzothiazole-2-amine (MBTA), and the effect of these parameters on their inhibition efficiency of corrosion of mild steel, using the quantum chemically calculated parameters. Parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap (ΔE), dipole moment (μ), electronegativity (χ), global hardness (η), softness (σ), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and $\Delta E_{Back-donation}$ have been calculated and compared with the experimental results. The Fukui functions and local softness (σ) values were utilized to elucidate the reactive sites in the studied molecule. The molecular and optimized structure of the inhibitors BTA and MBTA are shown in figure.1

MATERIALS AND METHODS

2.1 Quantum Chemical Calculation

The present quantum chemical calculations have been performed with Gaussian-03 series of program package [23]. In our calculation we have used Becke's three parameter exchange functional [24] along with the Lee–Yang–Parr nonlocal correlation functional (B3LYP) [25] using 6-311++G(d,p) basis set. Quantum chemical methods also have been proved to be a very powerful tool for studying inhibition of corrosion of the metals [26]. Frontier molecular orbital distribution was obtained and various molecular properties such as energy of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), energy gap ΔE , total electronic energy of the molecule and global reactivity parameters such as chemical hardness (η), chemical potential (μ) and electrophilicity index (ω) were also obtained to analyze the reactivity of the inhibitor molecules.

The basic relationship of the density functional theory of chemical reactivity is precisely, the one established by Parr *et al.*, [27] to the number of electrons, and therefore with the negative of the electronegativity χ .

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r)} = -\chi \quad (1)$$

Where μ is the electronic chemical potential, E is the total energy, N is the number of electrons, and $v(r)$ is the external potential of the system.

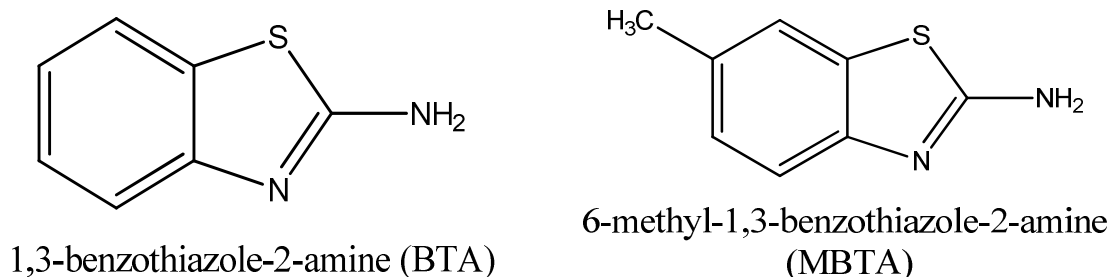


Figure 1. Names, molecular structure and the abbreviation of the inhibitors investigated

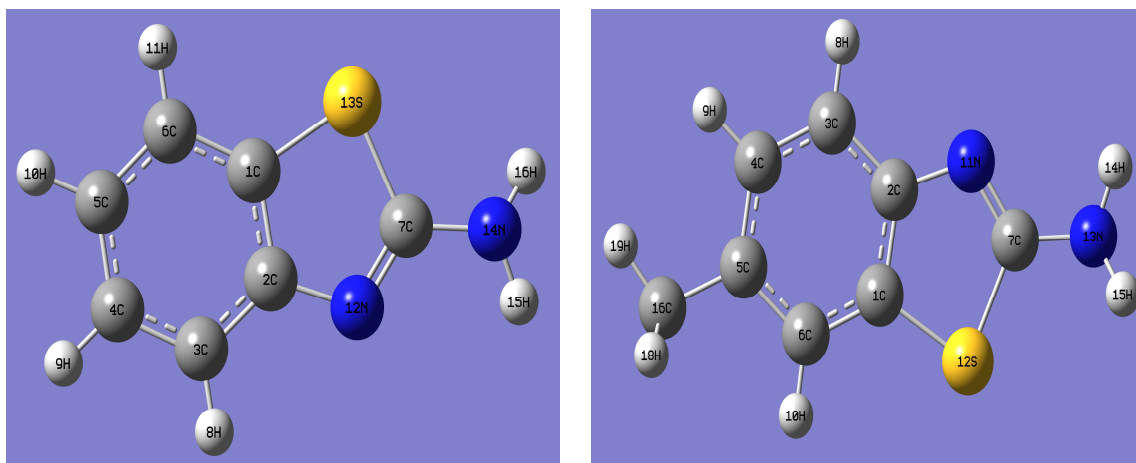


Figure 2. Optimized structure of BTA and MBTA calculated with the B3LYP/6-311++G(d,p)

The global chemical hardness (η) has been defined within the DFT as the second derivative of the E with respect to N as $v(r)$ property which measures both the stability and reactivity of the molecule [28].

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

where $v(r)$ and μ are, respectively, the external and electronic chemical potentials.

Molecular properties related to the reactivity and selectivity of the inhibitors like ionization potential (I), electron affinity (A), the electronegativity (χ), global hardness (η) and softness (σ), were estimated according to Koopman's theorem [29] which relates to the energy of the HOMO and the LUMO.

Ionization potential (I) is related to the energy of the E_{HOMO} through the equation:

$$I = -E_{\text{HOMO}} \quad (3)$$

Electron affinity (A) is related to E_{LUMO} through the equation:

$$A = -E_{\text{LUMO}} \quad (4)$$

When the values of I and A are known, one can determine the electronegativity χ and the global hardness (η).

The absolute electronegativity (χ) and absolute chemical hardness (η) of the inhibitor molecule are given [28]

$$\chi = \frac{I + A}{2} \quad (5)$$

$$\eta = \frac{I - A}{2} \quad (6)$$

Electron polarizability, also called as chemical softness (σ) is the measure of the capacity of an atom or group of atoms to receive electrons [30], it is estimated by using the equation:

$$\sigma = \frac{1}{\eta} \quad (7)$$

When two systems, Fe and inhibitor are brought together, electrons will flow from lower (χ) inhibitor to higher (χ) Fe, until the chemical potentials become equal. Therefore the fraction of electrons transferred (ΔN) from the inhibitor molecule to the metallic atom was calculated according to Pearson electronegativity scale [31].

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \quad (8)$$

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule respectively η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of $\chi_{Fe}=7.0$ eV/mol and $\eta_{Fe} = 0$ eV/mol for the computation of number of transferred electrons [31].

The absolute electrophilicity index (ω) [32] which is calculated by the equation

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

According to the definition, this index measures the propensity of chemical species to accept electrons. A high value of electrophilicity index describes a good electrophile while a small value of electrophilicity index describes a good nucleophile. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

The local selectivity of a corrosion inhibitor is best analyzed using the Fukui function [33]. Their values are used to identify which atoms in the inhibitors are more prone to undergo an electrophilic or a nucleophilic attack. The change in electron density is the nucleophilic $f^+(r)$ and electrophilic $f^-(r)$ Fukui functions, which can be calculated using the finite difference approximation as follows [34].

$$f_k^+ = q_{N+1} - q_N \quad (10)$$

$$f_k^- = q_N - q_{N-1} \quad (11)$$

where q_N , q_{N+1} and q_{N-1} are the electronic population of the atom k in neutral, anionic and cationic systems.

The local softness σ^+ and σ^- for an atom can be expressed as the product of the condensed Fukui function (f) and the global softness (σ), as follows [35]

$$\sigma^+ = (f^+) \sigma \quad (12)$$

$$\sigma^- = (f^-) \sigma \quad (13)$$

The local softness contains additional information about the total molecular softness, which is related to the biological reactivity.

According to the simple charge transfer model for donation and back-donation of charges proposed recently by Gomez *et al.*, [36] an electronic back-donation process might be occurring governing the interaction between the inhibitor molecule and the metal surface. The concept establishes that if both processes occur, namely charge transfer to the molecule and back-donation from the molecule, the energy change is directly related to the hardness of the molecule, as indicated in the following expression.

$$\Delta E_{\text{Back-donation}} = -\frac{\eta}{4} \quad (14)$$

The $\Delta E_{\text{Back-donation}}$ implies that when $\eta > 0$ and $\Delta E_{\text{Back-donation}} < 0$ the charge transfer to a molecule, followed by a back-donation from the molecule, is energetically favored. In this context, hence, it is possible to compare the stabilization among inhibiting molecules, since there will be an interaction with the same metal, then it is expected that it will decrease as the hardness increases.

RESULTS AND DISCUSSION

According to the frontier molecular orbital (FMO) theory, of chemical reactivity, transition of electron is due to interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species [37]. The energy of HOMO is often associated with the electron donating ability of a molecule. Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on mild steel and therefore better inhibition efficiency. When we compare the studied compounds BTA and MBTA the calculations show that the compound MBTA has the highest HOMO energy - 5.8057, implies the highest tendency to donate electrons. The various quantum chemical parameters are collected and reported in Table 1.

Table 1. The calculated quantum chemical parameters for the investigated inhibitors obtained with B3LYP/6-311++G(d,p) method

Parameters	MBTA	BTA
Total energy (au)	-817.510	-778.183
E_{HOMO} (eV)	-5.8057	-5.9681
E_{LUMO} (eV)	-0.5140	-0.5619
Energy gap(ΔE)	5.2917	5.4062
Ionization potential(I)	5.8057	5.9681
Electron affinity(A)	0.5140	0.5619
Hardness(η)	2.64585	2.7031
Electronegativity(χ)	3.15985	3.265
Softness (σ)	0.37795	0.36994
Electrophilicity index(ω)	1.88685	1.97185
Fraction of electron transferred (ΔN)	0.72569	0.69087
$\Delta E_{\text{backdonation}}$ (eV)	-0.66146	-0.67577

The energy gap ΔE , is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As ΔE decreases the reactivity of the molecule increases leading to increase of the inhibitor efficiencies [38]. When we examine the obtained values of energy gap, the results obtained show that the compound MBTA has a small ΔE , this means that the molecule could have better performance as corrosion inhibitor. It is shown from the calculation that there was no obvious correlation between the values of dipole moment with the trend of inhibition efficiency obtained experimentally. In the literature also there is a lack of agreement on the correlation between the dipole moment and inhibition efficiency [39,40]

Global hardness and global softness are the basic chemical concepts, called global reactivity descriptors which has been theoretically justified within the framework of DFT. A hard molecule has a large energy gap and a soft molecule has a small energy gap [41]. Soft molecules are more reactive than the hard molecules because they could easily offer electrons to an acceptor. In accordance with the HSAB principle, normally the molecule with least value of global hardness is expected to have the highest inhibition efficiency [42]. It is clear from the calculation that MBTA has the lowest hardness value and highest softness value is expected to be the best inhibitor.

The number of electrons transferred (ΔN) from the inhibitor to the iron was also calculated and tabulated in table.1. The values of ΔN show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [43]. If $\Delta N < 3.6$, the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface and it increases in the following order; MBTA>BTA. The results indicate that the ΔN value of MBTA is greater which strongly correlates with the experimental inhibition efficiencies.

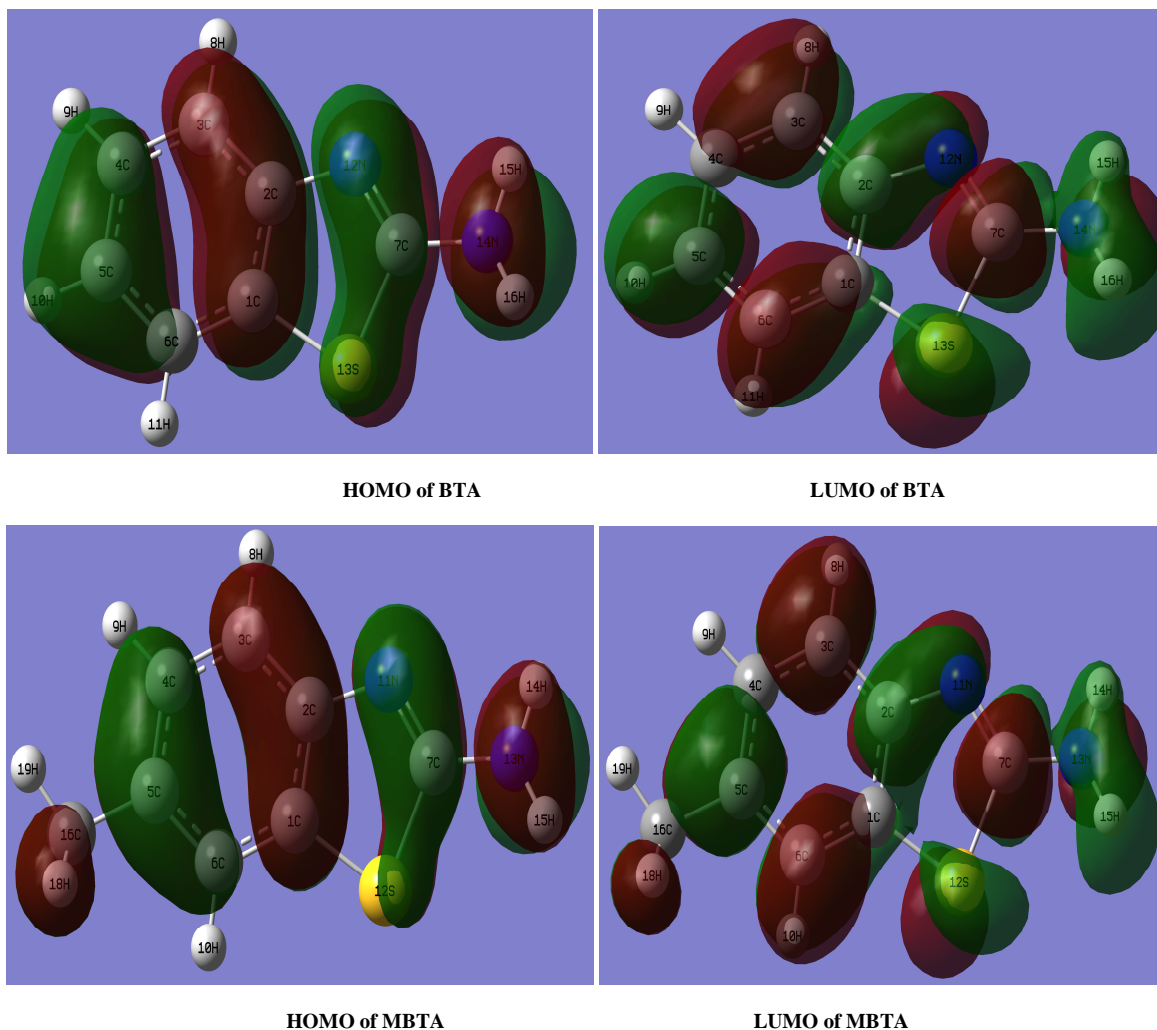


Figure 3.HOMO and LUMO diagrams of BTA and MBTA using B3LYP/6-311++G(d,p)

3.1 Local Selectivity

Fukui functions compute local reactivity indices that makes possible to rationalize the reactivity of individual molecular orbital contributions. The condensed Fukui function and local softness indices allow one distinguish each part of the molecule on the basis of its distinct chemical behaviour due to the different substituted functional group. The preferred site for nucleophilic attack is the atom in the molecule where the value of f_k^+ is maximum and it is associated with the LUMO energy while the site for electrophilic attack is controlled by the values of f_k^- which is associated with the HOMO energy. Fukui function depicted in table 2, implies that the atoms S13 and S12 are preferred site for electrophilic attack, as these sites have higher value of Fukui function f_k^- in the inhibitor BTA and MBTA. The atoms C7 in both the inhibitor are most susceptible sites for nucleophilic attack since these sites have the highest values of Fukui function f_k^+ .

The local softness contains the information similar to those condensed Fukui function plus additional information about the total molecular softness. A high value of σ^+ indicates high nucleophilicity and the high value of σ^- indicates high electrophilicity.

Table. 2 The selected Fukui and softness indices values for the inhibitors BTA and MBTA calculated with B3LYP/6-311++G(d,p)

Inhibitor	Atom	f_k^+	f_k^-	σ^+	σ^-
BTA	C(7)	0.18454	0.05238	0.10666	0.03027
	S(13)	0.17582	0.18240	0.10162	0.10542
	C(3)	0.079767	0.06347	0.04610	0.03668
MBTA	C(7)	0.18093	0.05373	0.10457	0.03105
	S(12)	0.162864	0.170318	0.09414	0.09843
	C(5)	0.014672	0.019795	0.00847	0.01144

CONCLUSION

The inhibition efficiency of BTA and MBTA has been investigated by utilizing quantum chemical approaches utilizing DFT method. The inhibition efficiency of BTA and MBTA obtained theoretically increased with increase in HOMO and decrease in energy gap. MBTA has the highest inhibition efficiency than BTA because it has the highest HOMO and lowest energy gap. Parameters like hardness (η), electronegativity (χ), softness (σ), chemical potential (μ), the fractions of electrons transferred (ΔN) and the electrophilicity index (ω) confirms the order of inhibition efficiencies : MBTA > BTA. The condensed Fukui functions agree on the possible electron rich and electron poor centres in the studied inhibitors. The presence of methyl group in MBTA, which is an electron donor, makes the benzene ring moiety possible to react with the metal d-orbital resulting in stronger adsorption in mild steel than BTA. The theoretically obtained inhibitor order gives good correlation with experimentally determined inhibition efficiency.

REFERENCES

- [1] D.Gopi, K.M.Govindaraju, V.C.A.Prakash, V.Manivannan and L. Kavitha, *J.Appl. Electrochem.*, **2009**, 39, 269.
- [2] A.S.Fouda, A.A.Al-Sarawy and E.E. El- Katori, *Desalination*. **2006**, 201, 1.
- [3] P. Udhayakala A. Jayanthi T. V. Rajendiran S. Gunasekaran, *Res. Chem. Intermed.*, **2013** 39, 895.
- [4] N.O. Eddy, S.A. Odoemelam, *Adv. Nat. Appl. Sci.*, **2008**, 2(1), 35.
- [5] S.A. Umoren, I.B. Obot, E.E. Ebenso, N.O. Obi-Egbedi, *Int. J. Electrochem. Sci.*, **2008**, 3, 1029.
- [6] Mwacham M. Kanbanda, Lutendo C. Murulana and Eno E. Ebenso, *Int.J.Electrochem.Sci.*, **2012** ,7, 179.
- [7] P.Hohenberg and W.Kohn, *Phys. Rev.*, **1964**, 136B, 864.
- [8] M.H.Cohen, In *Topics in Current Chemistry*, Nalewajski RF, Ed.; Springer-Verlag: Heidelberg, Germany, **1996**, 183, 143.
- [9] S .Gupta, N. Ajmera, N. Gautam, R Sharma and D.Gauatam, *Ind J Chem.*, **2009**, 48B,853.
- [10] B. Rajeeva, N.Srinivasulu, and Shantakumar, *E-Journal of Chemistry*, **2009**, 6(3),775.
- [11] H.L.K.Stanton, R. Gambari, H.C.Chung, C.O.T.Johny, C.Filly and S.C.C.Albert, *Bioorg Med . Chem*. **2008**, 16,3626.
- [12] M.Wang, M. Gao, B.Mock ,K. Miller,G. Sledge, G. Hutchins and Q. Zheng, *Bioorg Med Chem*.**2006**, 14, 8599.
- [13] S. Pattan, C. Suresh, V. Pujar, V. Reddy, V. Rasal and B. Koti, *Ind J Chem.* , **2005**, 44B, 2404.
- [14] J.S.Saggu, R.Sharma, H. Dureja and V.J. Kumar, *Indian Inst. Sci.*, **2002**, 82, 177.
- [15] H. T. Le, I. B. Lemaire, A. K.Gilbert, F. Jolicoeur, L.Yang and N.Leduc, *JPET*, **2004**, 309, 146.
- [16] K. G. Ayhan, C.Kus, T.Coban, Can, B. J.Eke, *Enzyme Inhib. Med. Chem.*, **2004**, 19(2), 129.
- [17] S. R.Nagarajan, C. G. A. De, D. P.Getman, H. F.Lu, J. A.Sikorski and J. L.Walker, *Bioorg. Med. Chem. Lett.*, **2003**, 11, 4769.
- [18] Ru Sun, Jianlin Yao, Shujin Li and Renao Gu, *Vib. Spectros.*, **2008**, 47(1), 38.
- [19] V. Sathyanarayanmoorthi, R. Karunathan, and V. Kannappan, *Journal of Chemistry***2013**, Article ID 258519, 14 pages
- [20] ChenJinCan, Qian Li, ShenYong, Chen LanMei and Zheng KangCheng, *Sci China Ser B-Chem.*, **2008**, 51, 111.
- [21] Mohamed, E.Musa, Taha and K. Kamal, *Nature & Science*, **2011**, 9(8), 34.
- [22] N. S. Patel, P. Beranek, M. Nebyla, M. Pribyl and D. Snita, *Int. J. Electrochem. Sci.*, **2014**, 9 3951.
- [23] M.J. Frisch, G.W.Trucks and H.B. Schlegel *et al.* Gaussian 03, Gaussian, Inc.: Pittsburgh PA, **2003**.
- [24] A. Becke, *J. Chem. Phys.*, **1993**, 98, 1372.

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- [25] C. Lee, W. Yang, and R. G. Parr, *Phys. Rev.*, **1988**, B 37, 785.
- [26] K.F. Khaled, K.Babic Samardzija and N.Hackerman, *Electrochim Acta*, **2005**, 50, 2515.
- [27] R.G.Parr, R.A. Donnelly, M. Levy and W.E. Palke, *J. Chem. Phys.*, **1978**, 68, 3801.
- [28] R.G. Parr and R.G. Pearson, *J. Am. Chem. Soc.*, **1983**, 105, 7512.
- [29] T.Koopmans, *Physica*, **1933**, 1, 104.
- [30] P. Senet, *Chem. Phys. Lett.*, **1997**, 275, 527.
- [31] R.G. Pearson, *Inorg.Chem.*, **1988**, 27, 734.
- [32] R.G. Parr, L. Szentpaly and S. Liu, *J.Am.Chem.Soc.*, **1999**, 121(9), 1922.
- [33] P. Fuentealba, P.Perez and R.Contreras, *J.Chem.Phys.*, **2000**, 113, 2544.
- [34] M.A. Quijano, Pardav A Cuan, M.R. Romo, G.N. Silva, R.A. Bustamante, A.R. Lopez and H.H. Hernandez, *Int. J. Electrochem. Sci.*, **2011**, 6, 3729.
- [35] S.R.Stoyanov, S. Gusarov, S.M. Kuznick and A. Kovalenko, *Mol.Simul.*, **2008**, 34, 943.
- [36] B.Gomez, N.V.Likhanova, M.A.Dominguez-Aguilar, R.Martinez-Palou, A.Vela and J.Gasquez, *J.Phy.Chem B*, **2006**, 110, 8928.
- [37] A.Y. Musa, A.H. Kadhum, A.B. Mohamad, A.B. Rohoma and H. Mesmari, *J.Mol.Struct.* **2010**, 969, 233.
- [38] M.K. Awad, M.S. Mustafa and M.M. Abo Elnga, *J.Mol.Struct.*, **2010**, 959(1-3), 66.
- [39] L.M. Rodriguez-Valdez, A. Martinez-Villfane, D. Glossman-Mitnik, *J.Mol.Struct. (THEO CHEM)*, **2005**, 713, 65.
- [40] A.Stoyanova, G.Petkova and S.D.Peyerimhoff, *Chem.Phys.*, **2002**, 279, 1.
- [41] N.O. Obi-Egbedi, I.B. Obot, M.I. El-Khaiary, S.A. Umoren and E.E. Ebenso, *Int. J. Electro Chem. Sci.*, **2011**, 6, 5649.
- [42] E.E. Ebenso, D.A. Isabirye and N.O. Eddy, *Int. J. Mol. Sci.*, **2010**, 11, 2473.
- [43] I. Lukovits, E. Kalman and F. Zucchi, *Corros.*, **2001**, 57, 3.