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DFT study on the adsorption mechanism of some phenyltetrazole substituted compounds as effective corrosion inhibitors for mild steel

P. Udhayakala[a*], A. Maxwell Samuel[b], T. V. Rajendiran[c] and S. Gunasekaran[d]

[a]*Department of Chemistry, Dr. MGR Educational and Research Institute, Chennai, India*
[b]*Department of Zoology, Nazareth Margoschis College, India*
[c]*Department of Chemistry, Pachaiyappa's College, Chennai, India*
[d]*Department of Physics, Spectrophysics Research Laboratory, Pachaiyappa's College, Chennai, India*

ABSTRACT

Corrosion inhibition performance of three Phenyltetrazole substituted compounds, namely 5-phenyl-1H-tetrazole (PT), 5-p-tolyl-1H-tetrazole (M-PT) and 5-(4-methoxyphenyl)-1H-tetrazole (MO-PT) on mild steel was evaluated by quantum chemical calculations based on density functional theory (DFT) method at the B3LYP/6-31G(d,P) basis set level in order to investigate the relationship between their molecular and electronic structure and inhibition efficiency. The quantum chemical properties most relevant to their potential action as corrosion inhibitors such as E_{HOMO}, E_{LUMO}, *energy gap* (ΔE), *dipole moment* (μ), *hardness* (η), *softness* (S), *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 condensed softness indices in order to compare the possible sites for nucleophilic and electrophilic attacks. The theoretical results obtained using DFT based reactivity indexes, were found to be consistent with the experimental outcomes.*

Keywords: Phenyltetrazole, Corrosion inhibition, DFT- derived indices, Fukui function, electrophilicity index.

INTRODUCTION

Corrosion of mild steel is an inevitable process that produces deterioration of materials and their properties resulting in massive economic losses especially when it's occur in aggressive media like hydrochloric acid [1]. The study of corrosion process and their inhibition by organic inhibitors is a very active field of research [2]. Most efficient inhibitors are organic compounds containing electronegative functional groups and π-electrons in triple or conjugated double bonds[3].A number of heterocyclic compounds containing nitrogen, oxygen and sulphur either in the aromatic or long chain carbon system have been reported as effective inhibitors of metal corrosion [4]. Researchers conclude that the adsorption on the metal surface depends mainly on the physicochemical properties of the inhibitor, such as the functional group, molecular electronic structure, electron density at the donor atom, π orbital character and the molecular size [5,6]. The power of the inhibition depends on the molecular structure of the inhibitor. Organic compounds, which can donate electrons to unoccupied d orbital of 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 [7].

Quantum chemical calculations have been widely used to evaluate the inhibition performance of corrosion inhibitors and the reaction mechanism. They have been proved to be a very powerful tool for studying corrosion inhibition mechanism [8-10]. Density functional theory (DFT) [11,12] has provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes [13-15]. A variety of chemical concepts which are now widely used as descriptors of chemical reactivity, e.g., electronegativity [14] hardness or softness quantities etc., appear naturally within DFT [11]. The Fukui function [15] representing the relative local softness of the electron, measures the local electron density/population displacements corresponding to the inflow of a single electron. They have been successfully performed to link the corrosion inhibition efficiency with molecular orbital (MO) energy levels for some kinds of organic compounds [16, 17].

Tetrazole and its derivatives have important applications in major areas, such as medicine, agriculture and imaging technology. They have attracted much attention because of their unique structure and applications as antihypertensive, antiallergic, antibiotic and anticonvulsant agents as well as in cancer and AIDS treatment [18-23]. The tetrazole functional group has currently been received considerable attention because of a wide range of applications such as corrosion inhibitors [24].

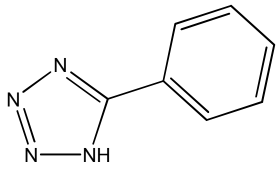
Pengju Liu *et al.* have studied the electrochemical and quantum chemical properties of 5-substituted tetrazoles as corrosion inhibitors for copper [25]. 1,2,3,4-tetrazole (TTZ) and some of its derivatives has been analysed by M. Mihit *et.al.*[26]. The inhibitive effect of some tetrazole derivatives towards Aluminium has been studied by K.F. Khaleda and M.M. Al-Qahtani[27].

Although experimental work of Elkacimi *et al.* [28] provide valuable information on the corrosion inhibition efficiency of Phenyltetrazole substituted compounds, namely 5-phenyl-1H-tetrazole (PT), 5-p-tolyl-1H-tetrazole (M-PT) and 5-(4-methoxyphenyl)-1H-tetrazole (MO-PT), a deep understanding of the inhibition property remain unclear. The objective of the present paper is to extend the study of Elkacimi, *et al.* [28] by analyzing the inhibition efficiency of PT, M-PT and MO-PT on theoretical chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), ionization potential (I), electron affinity (A), electro negativity (χ), global hardness (η), softness (S), the global electrophilicity index (ω), the fraction of electrons transferred (ΔN) and back donation(ΔE). The local reactivity has been analyzed by means of the Fukui indices, since they indicate the reactive regions, in the form of the nucleophilic and electrophilic behaviour of each atom in the molecule using DFT calculations.

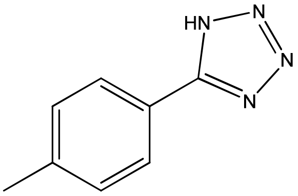
MATERIALS AND METHODS

2.1 Quantum Chemical Calculation

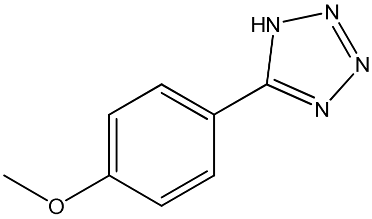
In order to explore the theoretical-experimental consistency, quantum chemical calculations were performed using Gaussian-03 software package [29]. Complete geometrical optimizations of the investigated molecules are performed using density functional theory(DFT) with the Becke's three parameter exchange functional along with the Lee– Yang–Parr nonlocal correlation functional (B3LYP) [30,31]. The calculations were based on 6-31G (d,p) basis set. This method has been widely implemented to study the relationship between corrosion inhibition efficiency of the molecules and their electronic properties [32]. Recently, Density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/ surface mechanism and to describe the structural nature of the inhibitor in the corrosion process [33]. The chemical and optimized structures of the compounds studied are given in Fig 1. and Fig 2.



5-phenyl-1H-tetrazole(PT)

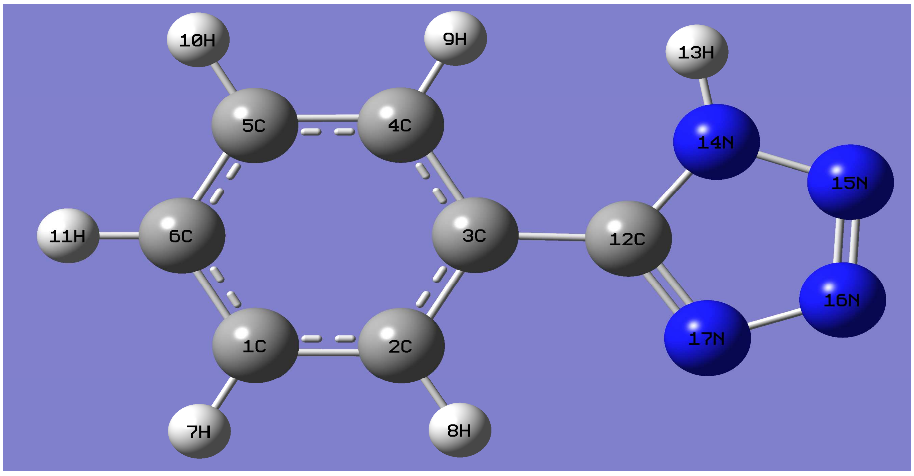


5-p-tolyl-1H-tetrazole(M-PT)

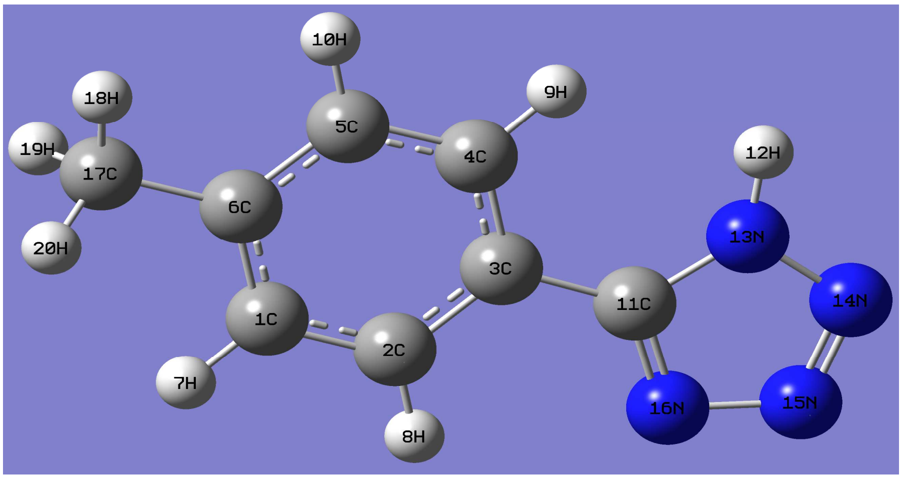


5-(4-methoxyphenyl)-1H-tetrazole(MO-PT)

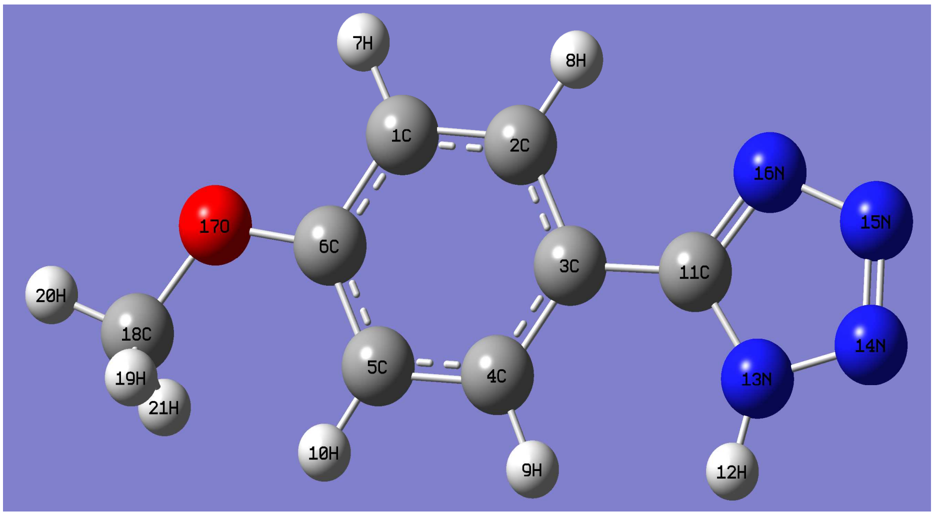
Figure 1. Names, molecular structure and the abbreviation of the inhibitors investigated



PT



M-PT



MO-PT

Figure 2. Optimized structure of PT, M-PT and MO-PT calculated with the B3LYP/6-31G(d,p)

2.2. Theoretical background

Global quantities

Density functional theory (DFT) [11] has been found to be successful in providing theoretical insights into the chemical reactivity and selectivity, in terms of popular qualitative chemical concepts like electronegativity (χ), hardness (η), softness(S), electrophilicity index(ω) and local reactivity descriptors such as Fukui function, F(r) and local softness, s(r).

The basic relationship of the density functional theory of chemical reactivity is precisely, the one established by *Parr et al.*, [34], that links the chemical potential of DFT with the first derivative of the energy with respect to the number of electrons, and therefore with the negative of the electronegativity χ.

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

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

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 [35].

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

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

According to Koopman's theorem [36], ionization potential *(I)* and electron affinity *(A)* the electronegativity(χ), global hardness(η) and softness *(S)*, may be defined in terms of the energy of the HOMO and the LUMO.

Ionization potential (I) is defined as the amount of energy required to remove an electron from a molecule [37]. It is related to the energy of the E_{HOMO} through the equation:

$$I = -E_{HOMO} \tag{3}$$

Electron affinity (A) is defined as the energy released when a proton is added to a system [37]. It is related to E_{LUMO} through the equation:

$$A = -E_{LUMO} \tag{4}$$

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

The electronegativity is the measure of the power of an atom or group of atoms to attract electrons towards itself [38], it can be estimated by using the equation:

$$\chi = \frac{I + A}{2} \tag{5}$$

Chemical hardness (η) measures the resistance of an atom to a charge transfer [39], it is estimated by using the equation:

$$\eta = \frac{I - A}{2} \tag{6}$$

Chemical softness (S) is the measure of the capacity of an atom or group of atoms to receive electrons [39], it is estimated by using the equation:

$$S = \frac{1}{\eta} \tag{7}$$

For a reaction of two systems with different electronegativities the electronic flow will occur from the molecule with the lower electronegativity (the organic inhibitor) towards that of higher value (metallic surface), until the chemical potentials are equal [40]. Therefore the fraction of electrons transferred (ΔN) from the inhibitor molecule to the metallic atom was calculated according to Pearson electronegativity scale [41]

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{\left[2(\eta_{Fe} + \eta_{inh}\right]} \tag{8}$$

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 [42] and $\eta_{Fe} = 0$ by assuming that for a metallic bulk I = A [43] because they are softer than the neutral metallic atoms.

The electrophilicity is a descriptor of reactivity that allows a quantitative classification of the global electrophilic nature of a molecule within a relative scale. Parr *et al* [44] have proposed electrophilicity index as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index(ω) as follows.

$$\omega = \frac{\mu^2}{2\eta} \tag{9}$$

According to the definition, this index measures the propensity of chemical species to accept electrons. A good, more reactive, nucleophile is characterized by lower value of μ, ω; and conversely a good electrophile is characterized by a high value of μ, ω. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

2.3. Local molecular reactivity

Fukui functions were computed since it provides an avenue for analyzing the local selectivity of a corrosion inhibitor [45]. 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 [46].

$$f_k^{+} = q_{N+1} - q_N \tag{10}$$

$$f_k^{-} = q_N - q_{N-1} \tag{11}$$

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

Condensed softness indices allowing the comparison of reactivity between similar atoms of different molecules can be calculated easily starting from the relation between the Fukui function $f(r)$ and the local softness $s(r)$ [47]

$$s(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} = f(r)S \tag{12}$$

From this relation, one can infer that local softness and Fukui function are closely related, and they should play an important role in the field of chemical reactivity.

According to the simple charge transfer model for donation and back-donation of charges proposed recently by Gomez *et al*., [48] 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.

$$\Delta E_{\text{Back-donation}} = -\frac{\eta}{4} \tag{13}$$

The $\Delta E_{Back\text{-}donation}$ implies that when $\eta > 0$ and $\Delta E_{Back\text{-}donation} < 0$ 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 theory (FMO) 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 [49]. The energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency towards the donation of electron by 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. E_{LUMO} indicates the ability of the molecule to accept electrons. The binding ability of the inhibitor to the metal surface increases with increasing HOMO and decreasing LUMO energy values. Frontier molecular orbital diagrams of PT,M-PT and MO-PT is represented in fig. 3.

Table 1. Quantum chemical parameters for PT,M-PT and MO-PT calculated using B3LYP/6-31G(d,p).

Parameters	PT	M-PT	MO-PT
E_{HOMO}(eV)	-6.93797	-6.70204	-6.28488
E_{LUMO} (eV)	-1.54374	-1.43706	-1.25338
Energy gap(ΔE) (eV)	5.39423	5.26498	5.0315
Dipole moment (Debye)	5.9427	6.4287	7.6171

E_{HOMO} is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy[50]. The inhibitor does not only donate electron to the unoccupied d orbital of the metal ion but can also accept electron from the d-orbital of the metal leading to the formation of a feedback bond.

From table 1, it can be clearly seen that the E_{HOMO} for the three compounds follow the order as MO-PT>M-PT>PT. The highest value of -6.28488(eV) of MO-PT indicates the better inhibition efficiency than the other compounds.

The gap between the E_{HOMO} and E_{LUMO} energy levels of the molecules 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 in the %IE of the molecule. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low [51]. Hard molecules have high HOMO-LUMO gap [52] and thus soft bases inhibitors are the most effective for metals [53]. The value of ΔE indicated in table 1 show the following relation ; PT> M-PT> MO-PT, which suggests that the inhibitor MO-PT has the lowest energy gap and highest reactivity in comparison to the other compounds, could have better performance as corrosion inhibitor.

The dipole moment (μ in Debye) is another important electronic parameter that results from non uniform distribution of charges on the various atoms in the molecule. The high value of dipole moment probably increases the adsorption between chemical compound and metal surface [54]. The energy of the deformability increases with the increase in μ, making the molecule easier to adsorb at the Fe surface. The volume of the inhibitor molecules also increases with the increase of μ. This increases the contact area between the molecule and surface of iron and increasing the corrosion inhibition ability of inhibitors. In our study the value 7.6171(Debye) of MO-PT enumerates its better inhibition efficiency.

Ionization energy is a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of the atoms and molecules [55]. The low ionization energy 6.28488 (eV) of MO-PT indicates the high inhibition efficiency.

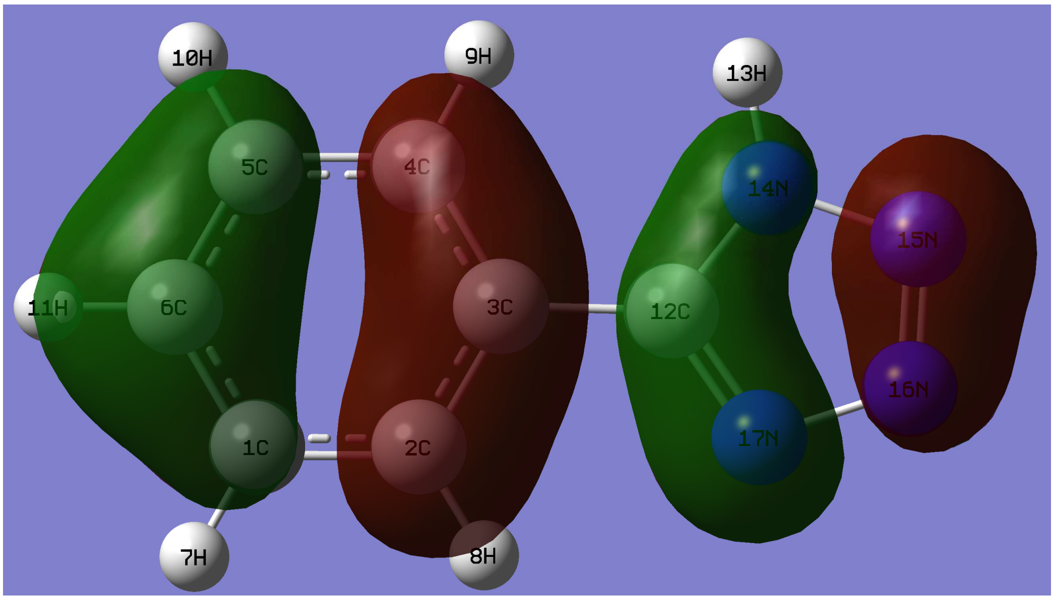
Hardness and softness are the basic chemical concepts, called global reactivity descriptors and has been theoretically justified within the framework of density functional theory(DFT) [11].These are the important properties to measure the molecular stability and reactivity. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [56]. In our present study MO-PT with low hardness value 2.51575(eV) compared with other compounds have a low energy gap. Normally, the inhibitor with the least value of global hardness (hence the highest value of global softness) is expected to have the highest inhibition efficiency [57]. For the simplest transfer of electron, adsorption could occur at the part of the molecule where softness(S), which is a local property, has a highest value [58]. MO-PT with the softness value of 0.397496 has the highest inhibition efficiency.

Table 2. Quantum chemical parameters for PT, M-PT and MO-PT calculated using B3LYP/6-31G(d,p)

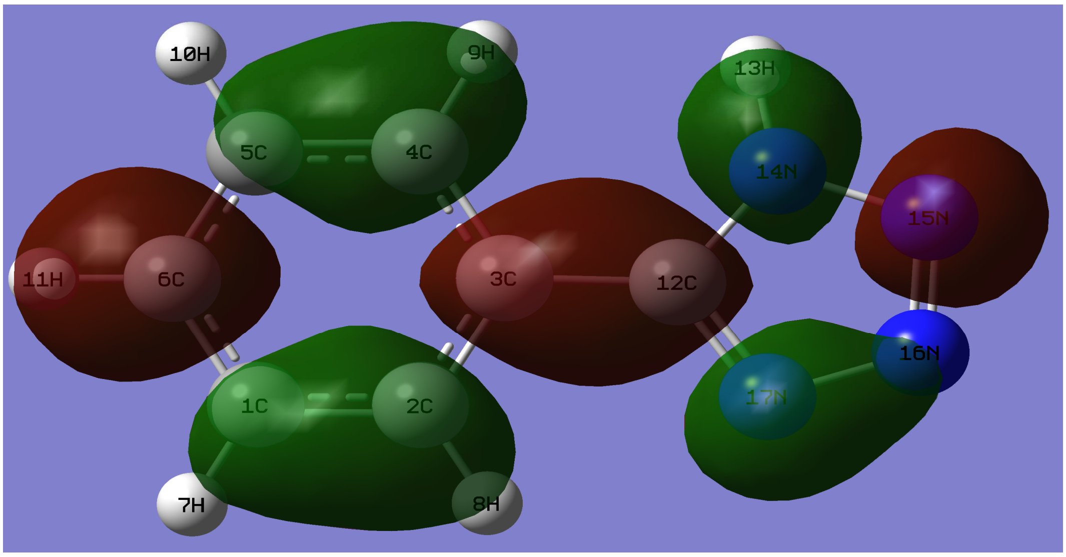
Parameters	PT	M-PT	MO-PT
E_N (au)	-489.32634	-528.64770	-603.85278
IE(eV)	6.93797	6.70204	6.28488
EA(eV)	1.54374	1.43706	1.25338
η (eV)	2.69712	2.63249	2.51575
S (eV)	0.370766	0.379868	0.397496
χ (eV)	4.24086	4.06955	3.76913
ω	3.33409	3.14555	2.82348
μ	-4.24086	-4.06955	-3.76913

The table 2 shows the order of electronegativity as PT >M-PT>MO-PT. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order MO-PT> M-PT> PT. According to Sanderson's electronegativity equalization principle [59], PT with a high electronegativity and low difference of electronegativity quickly reaches equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency.

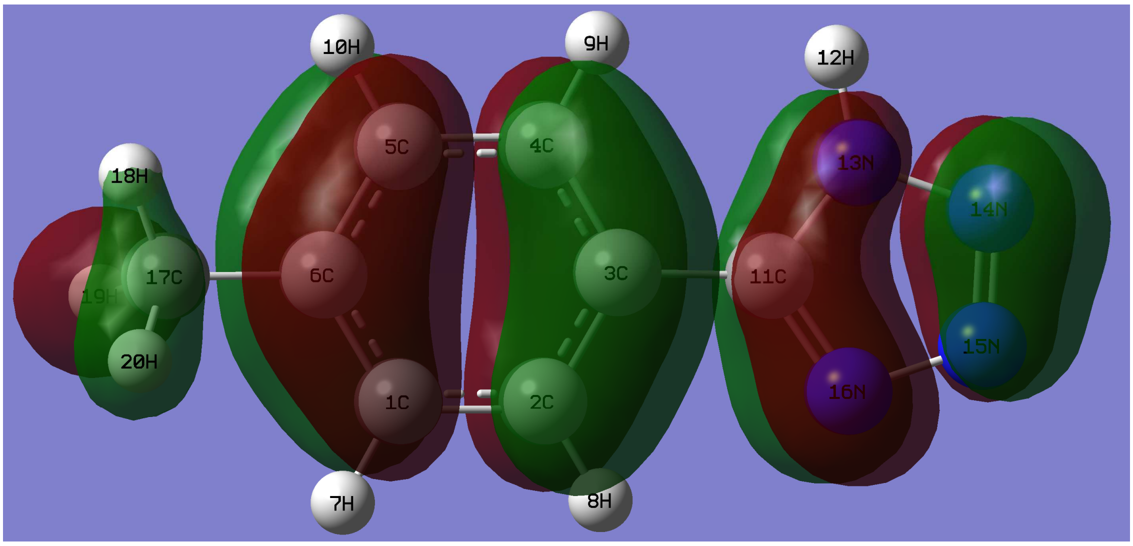
Global electrophilicity index (ω) is the measure of the electrophilic tendency of a molecule. In our case, the inhibitor MO-PT with low electrophilicity index value than the other compounds, has the highest inhibition efficiency.



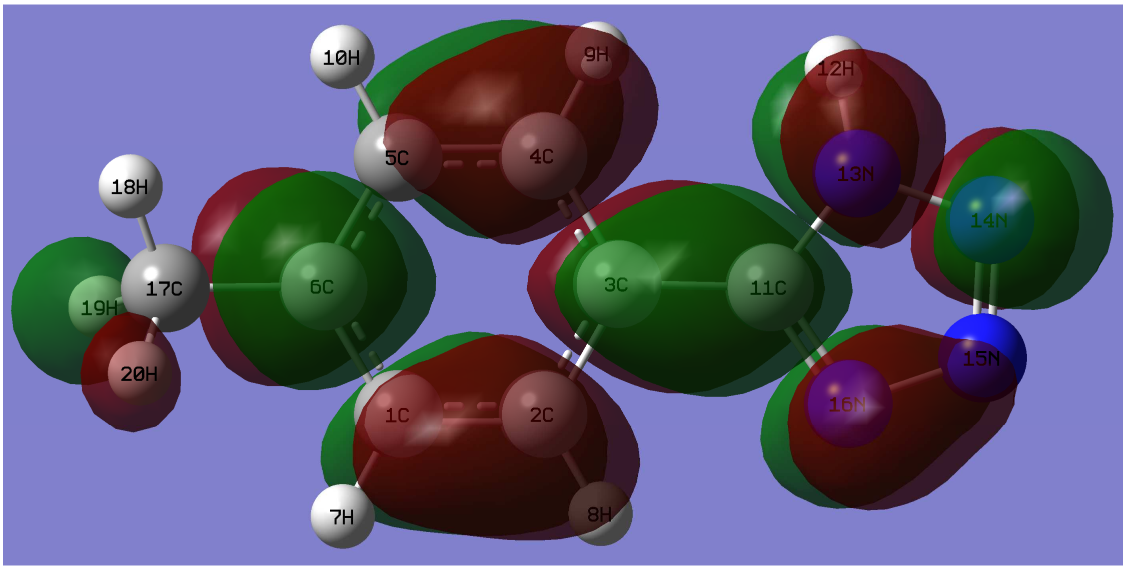
HOMO of PT



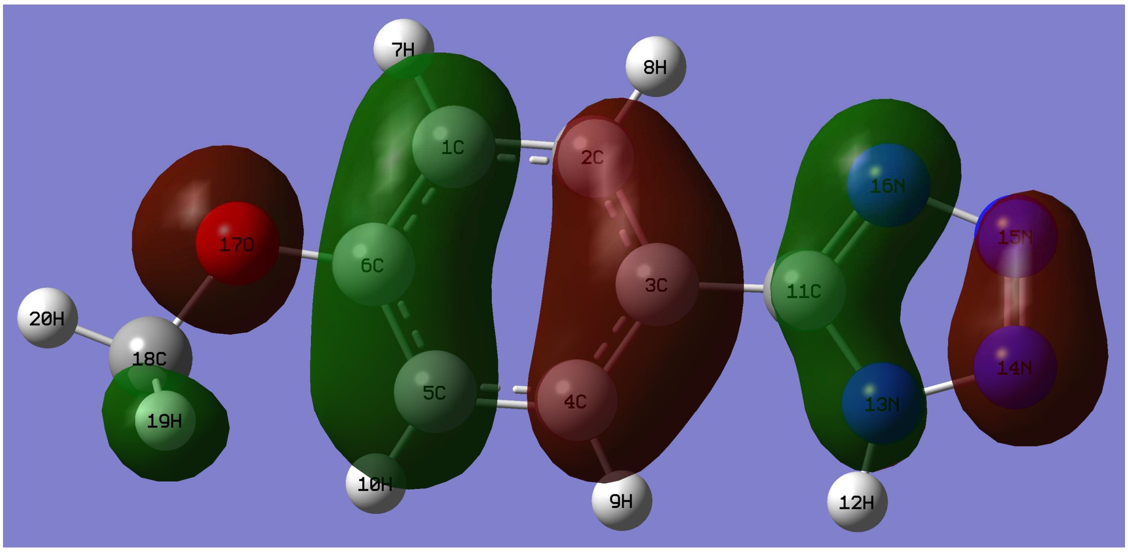
LUMO of PT



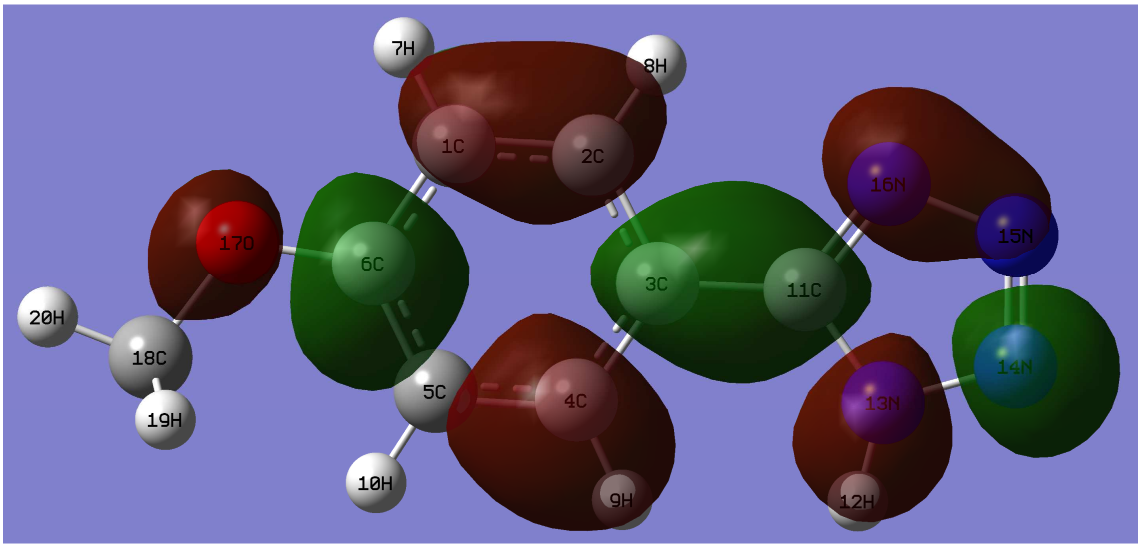
HOMO of M-PT



LUMO of M-PT



HOMO of MO-PT



LUMO of MO-PT

Figure 3. Frontier molecular orbital diagrams of PT, M-PT and MO-PT by B3LYP/6-31G(d,p)

The number of electrons transferred (Δ*N*) and *back-donation(ΔE)* was also calculated and tabulated in Table 3. Values of Δ*N* show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [60]. If Δ*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: PT < M-PT<MO-PT. The results indicate that Δ*N* values correlates strongly with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is associated with the best inhibitor (MO-PT), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (PT).

Table 3. The number of electron transferred (Δ*N*) and *ΔE* back donation (eV) calculated for inhibitor PT and M-PT and MO-PT .

Parameters	PT	M-PT	MO-PT
Transferred electrons fraction (ΔN)	0.511497	0.556593	0.642128
ΔE back-donation / (eV)	-0.67428	0.65812	-0.62894

There is a general consensus by several authors that the more negatively charged a heteroatom, is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction [61]. It is important to consider the situation corresponding to a molecule that is going to receive a certain amount of charge at some centre and is going to back donate a certain amount of charge through the same centre or another one [50]. Parr and Yang proposed that larger value of Fukui function indicate more reactivity [15]. Hence greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule.

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 f_k^+, measures the changes of density when the molecules gains electrons and it corresponds to reactivity with respect to nucleophilic attack. On the other hand, f_k^- corresponds to reactivity with respect to electrophilic attack or when the molecule loss electrons. The calculated Fukui functions for the molecules PT, M-PT and MO-PT are presented in Tables 4,5 and 6.

According to fukui indices, C12 is the most reactive site for nucleophilic attack and H9 is the site of electrophilic attack in the compound PT. In the inhibitor M-PT, N16 is the site of nucleophilic attack and C11 is the site of electrophilic attack. The preferred site for attack by nucleophilic agent in the inhibitor MO-PT is at the site C11 and electrophilic attack is at H9.

Table 4. Fukui and local softness indices for nucleophilic and electrophilic attacks in PT atoms calculated from Mulliken atomic charges ; Maxima in bold

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	-0.002286	0.021341	-0.000847	0.007913
2 C	0.053847	0.037175	0.019965	0.013783
3 C	0.029997	0.007185	0.011122	0.002664
4 C	0.01416	0.069363	0.005250	0.025717
5 C	0.008282	0.01744	0.003071	0.006466
6 C	0.058533	0.052351	0.021702	0.019410
7 H	0.085682	0.078446	0.031768	0.029085
8 H	0.118313	0.011153	0.043867	0.004135
9 H	0.009846	**0.132024**	0.003650	**0.048950**
10 H	0.079114	0.084179	0.029333	0.031211
11 H	0.091173	0.090379	0.033804	0.033509
12 C	**0.136345**	0.021013	**0.050552**	0.007791
13 H	0.055362	0.05233	0.020526	0.019402
14 N	0.019617	0.035361	0.007273	0.013111
15 N	0.131524	0.103371	0.048765	0.038327
16 N	0.052892	0.082528	0.019611	0.030598
17 N	0.057598	0.10436	0.021355	0.038693

Table 5. Fukui and local softness indices for nucleophilic and electrophilic attacks in M-PT atoms calculated from Mulliken atomic charges ; maxima in bold

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	0.012596	0.027409	0.004785	0.010412
2 C	0.057289	0.032610	0.021762	0.012387
3 C	-0.035081	0.072938	-0.013326	0.027707
4 C	0.034339	0.039992	0.013045	0.015192
5 C	0.022091	0.022298	0.008392	0.008470
6 C	0.010706	0.045373	0.004067	0.017236
7 H	0.082885	0.070307	0.031485	0.026707
8 H	0.09476	0.032285	0.035997	0.012264
9 H	0.03948	0.096642	0.014997	0.036711
10 H	0.075902	0.076516	0.028833	0.029066
11 C	-0.197601	**0.348635**	-0.075063	**0.132435**
12 H	0.078133	0.022693	0.029680	0.008620
13 N	0.112593	-0.064586	0.042771	-0.024534
14 N	0.135295	0.086729	0.051394	0.032946
15 N	0.088117	0.03744	0.033473	0.014222
16 N	**0.236959**	-0.087339	**0.090013**	-0.033177
17 C	-0.004206	-0.028382	-0.001597	-0.010781
18 H	0.048556	0.047242	0.018445	0.017946
19 H	0.059196	0.061672	0.022487	0.023427
20 H	0.047991	0.059526	0.018230	0.022612

Table 6 Fukui and local softness indices for nucleophilic and electrophilic attacks in MO-PT atoms calculated from Mulliken atomic charges ; maxima in bold

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	-0.005654	0.034886	-0.002247	0.013867
2 C	0.035445	0.027106	0.014089	0.010775
3 C	0.02147	0.009803	0.008534	0.003896
4 C	0.039394	0.058267	0.015659	0.023161
5 C	-0.032971	0.033372	-0.013106	0.013265
6 C	0.116743	0.03694	0.046405	0.014683
7 H	0.077606	0.073291	0.030848	0.029133
8 H	0.064923	0.009536	0.025806	0.003791
9 H	0.050902	**0.127865**	0.020233	**0.050826**
10 H	0.065324	0.072594	0.025966	0.028856
11 C	**0.138863**	0.015238	**0.055197**	0.006057
12 H	0.051719	0.041693	0.020558	0.016573
13 N	0.015056	0.02375	0.005985	0.009441
14 N	0.126765	0.081708	0.050388	0.032478
15 N	0.049395	0.062981	0.019634	0.025035
16 N	0.052103	0.076246	0.020711	0.030307
17 O	0.036943	0.085611	0.014685	0.034031
18 C	-0.046444	-0.045839	-0.018461	-0.018221
19 H	0.040872	0.056249	0.016246	0.022358
20 H	0.063854	0.062332	0.025382	0.024777
21 H	0.037691	0.056373	0.014982	0.022408

CONCLUSION

From the present study, we can deduce the following conclusions:

1. Through DFT calculations a correlation between parameters related to the electronic and molecular structures of three Phenyltetrazole substituted compounds, namely 5-phenyl-1H-tetrazole (PT), 5-p-tolyl-1H-tetrazole (M-PT) and 5-(4-methoxyphenyl)-1H-tetrazole (MO-PT) and their ability to inhibit the corrosion process could be established.

2. The calculated HOMO energy, energy gap(ΔE) and the value of dipole moment show reasonably good correlation with the efficiency of corrosion inhibition.

3. The parameters like hardness(η), Softness(S), dipole moment(μ), electron affinity(EA) ionization potential(IE), electronegativity(χ) and the fraction of electron transferred (ΔN) confirms the inhibition efficiency in the order of MO-PT>M-PT>PT.

4. Fukui function shows the nucleophilic and electrophilic attacking sites in the MO-PT,M-PT and PT**.**

5. Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

REFERENCES

[1] Z.El Adnani, M.Mcharfi, M.Sfaira, A.T. Benjelloum, M.Benzakour,M.Ebn Touhami, B.Hammouti and M.Taleb, *Int.J.Electrochem.Sci.*, **2012**,7, 3982.
[2] M. Bouayed, H. Rabba, A. Srhiri, J.Y. Saillard, A. Ban Bachir and A .Le Beuze, *Corros.Sci.*, 1**998,** 41(3), 501.
[3] P.Udhayakala, T.V.Rajendiran and S.Gunasekaran, *J.Comput. Method.Mol.Design*, **2012**, 2(1), 1.
[4] A.S. Fouda and A.S. Elithy, *Corros.Sci*., **2009**, 51(4) , 868.
[5] I.B. Obot and N.O. Obi-Egbedi, *Surface Review and Letters*, **2008**, 15(6), 903.
[6] H. Ju, Z.P. Kai and Y. Li, *Corros. Sci*., **2008**, 50, 865.
[7] P. Udhayakala, T.V. Rajendiran and S. Gunasekaran, *Der Pharmacia Lettre*, **2012**, 4 (4),1285.
[8] P. Choa, Q. Liang and Y. Li, *Appl. Surf. Sci*., **2005**, 252, 1596.
[9] F. Bentiss, M. Lebrini and M. Lagrenee, *Corros. Sci*., **2005**, 47, 2915.
[10] J. Vosta and J. Eliasek, *Corros. Sci*., **1971**, 11, 223.
[11] P. Hohenberg and W. Kohn, *Phys. Rev*., **1964**,136, B864-B871.
[12] R.G. Parr and W Yang, *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, **1989.**
[13] M.H. Cohen, *In Topics in Current Chemistry*; R.F.Nalewajski, Ed.; Springer-Verlag: Heidelberg, Germany, **1996**, 183, 143.
[14] R.T. Sanderson, *J. Am. Chem. Soc*., **1952**, 74, 272.
[15] R.G. Parr and W. Yang, *J. Am. Chem. Soc*., **1984**, 106, 4049.
[16] J. Fang and J. Li, *J .Mol. Struct.* (THEOCHEM), **2002**, 593, 179.
[17] T. Arslan, F. Kandemirli, E.E. Ebenso, I. Love and H. Alemu, *Corros Sci*., **2009**, 51, 35.
[18] L.V. Myznikov, A. Hrabalek, G. I. Koldobskii, *Chem. Het.Compounds*, **2007**, 43, 1.
[19] T. Mavromoustakos , A. Kolocouris, M. Zervou , P. Roumelioti , J. Matsoukas, R. Weisemann, *J. Med. Chem.*,**1999**, 42, 1714.
[20]Y. Tamura, F. Watanabe, T. Nakatani, K. Yasui, M. Fuji, T. Komurasaki, H. Tsuzuki, R. Maekawa, T.Yoshioka, K. Kawada, K. Sugita, M. Ohtani, *J. Med. Chem.*, **1998**, 41, 640- 649.
[21] M. J. Schocken, R. W. Creekmore, G.Theodoridis, G. J. Nystrom, R. A. Robinson, *Appl.Environ. Microbiol.*, **1989**, 55(5), 1220.
[22] S. J. Lim , Y. Sunohara, H. Matsumoto, *J. Pestic. Sci.*, **2007**, 32, 249.
[23] N. Mekni, A. Bakloiti, *J. Fluorine. Chem.*, **2008**, 129, 1073.
[24] S. Kertit, B. Hammouti, *App. Sur. Sci.*, **1996**, 93, 59. (b) E. Szoes, I. Bako, T. Kosztolanyi, I. Bertoti, E. Kalman, *Elctro.Chem. Acta.*, **2004**,49, 1371.
[25] Pengju Liu, Xia Fang, Yongming Tang, Chunning Sun and Cheng Yao, *Materials Sciences and Applications*, **2011**, 2, 1268.
[26] M. Mihit, K. Laarej, H. Abou El Makarim, L. Bazzi, R. Salghi , B. Hammouti, *Arabian Journal of Chemistry*, **2010**, 3, 55.
[27] K.F. Khaleda, M.M. Al-Qahtani, *Materials Chemistry and Physics*, **2009**, 113,150.
[28] Y. Elkacimi, M. Achnin, Y. Aouine, M. Ebn Touhami, A. Alami,R. Touir, M. Sfaira, D. Chebabe, A. Elachqar, B. Hammouti, *Portugaliae Electrochimica Acta, **2012**, 30(1), 53.*
[29] M.J. Frisch, G.W. Trucks and H.B. Schlegel *et al*. Gaussian 03, Gaussian, Inc.: Pittsburgh PA, **2003**.
[30] A.D. Becke, *J. Chem. Phys*., **1993**, 98, 1372
[31] C. Lee, W. Yang and R.G. Parr, *Phys. Rev.*, **1988**, *B* 37, 785.
[32] D.C. Young, **2001** *A practical guide for applying techniques to realworld problems in Computational Chemistry* (New York: JohnWiley & Sons Inc.) p. 630.
[33] M. Lashkari and M.R. Arshadi, *Chem. Phys*., **2004**, 299, 131.
[34] R.G. Parr, R.A. Donnelly, M. Levy and W.E. Palke, *J. Chem. Phys*., **1978,** 68, 3801.

[35] R.G. Parr and R.G. Pearson, *J. Am. Chem. Soc*., **1983**, 105, 7512.
[36] P. Geerlings, F. De Proft and W Langenaeker, *Chem. Rev*., **2003,** 103, 1793.
[37] J.B. Foresman, A Frisch, Exploring Chemistry with Electronic Structure Methods. Gaussian, Inc., Pittsburg, PA (USA), **1995**.
[38] L. Pauling, The Nature of the Chemical Bond. Cornell University Press, Ithaca, New York; **1960.**
[39] P. Senet, *Chem. Phys. Lett*., **1997,** 275, 527.
[40] S. Martınez, *Mater. Chem. and Phys*., **2002**, 77, 97.
[41] R.G. Pearson, *Inorg.Chem*., **1988**, 27, 734.
[42] V.S. Sastri and J.R. Perumareddi, *Corros. Sci*, **1997**, 53, 617.
[43] M.J.S. Dewar and W. Thiel, *J.Am.Che.Soc.*, **1977**, 99**,** 4899.
[44] R.G. Parr, L. Szentpaly and S. Liu , *J.Am.Chem.Soc.*, **1999**, 121,1922.
[45] A.A. Siaka, N.O. Eddy, S.O. Idris and L. Magaji , *Research J. Appl. Sci*., **2011,** 6(7-120), 487.
[46] 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.
[47] H. Wang, X. Wang, H. Wang. L. Wang and A. Liu, *J. Mol. Model*., **2007**, 13, 147.
[48] B. Gomez, N.V. Likhanova, M.A. Dominguez-Aguilar, R. Martinez-Palou, R. Vela and J. Gasquez, *J.Phy.Chem B*, **2006**, 110, 8928.
[49] A.Y. Musa, A.H. Kadhum, A.B. Mohamad, A.B. Rohoma and H. Mesmari, *J.Mol.Struct.*, **2010**, 969, 233.
[50] G. Gece and S. Bilgic, *Corros.Sci*., **2009**, 51, 1876.
[51] I.B. Obot, N.O. Obi-Egbedi and S.A. Umoren, *Int. J. Electro Chem. Sci*., **2009**, 4, 863.
[52] M.K. Awad, M.S. Mustafa and M.M Abo Elnga, *J.Mol.Struct.*, **2010**, 959(1-3), 66.
[53] X. Li, S. Deng, H. Fu and T. Li, *Electrochim. Acta*, **2009**, 54, 4089.
[54] M.A. Quraishi and R. Sardar, *J.Appl.Electrochem*., **2003**, 33(12), 1163.
[55] Sandip K Rajak, Nazmul Islam and Dulal C Ghosh, *J.Quantum information Science*, **2011**, 1, 87.
[56] 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.
[57] E.E. Ebenso, D.A. Isabirye and N.O. Eddy, *Int. J. Mol. Sci*., **2010**, 11, 2473.
[58] R. Hasanov, M. Sadikglu and S.Bilgic, *Appl. Surf. Sci*. **2007**, 253**,** 3913.
[59] P. Geerlings and F. De Proft, *Int. J. Mol. Sci.,* **2002**, 3, 276.
[60] I. Lukovits, E. Kalman and F. Zucchi, *Corrosion*, **2001**, 57, 3.
[61] G. Breket, E. Hur and C. Ogretir, *J.Mol.Stru.*,**2002**, 578, 79.