

Short Communication

Theoretical Studies on Mild Steel Corrosion Inhibition by 5-Substituted 1H-Tetrazoles in Acidic Media

Mahmud Ibrahim Elusta¹, Murat Alper Başaran², Fatma Kandemirli^{3,*}

¹ Metallurgy and Materials Engineering, Faculty of Engineering and Architecture, Kastamonu University, 37150, Kastamonu, Turkey.

² Alanya Alaaddin Keykubat University, Faculty of Engineering, Department of Management Engineering, 07425, Antalya, Turkey.

³ Department of Biomedical Engineering, Faculty of Engineering and Architecture, Kastamonu University, 37150, Kastamonu, Turkey.

*E-mail: fkandemirli@yahoo.com

¹E-mail: Elustam@gmail.com

Received: 20 July 2018 / Accepted: 14 September 2018 / Published: 7 February 2019

In this theoretical study, calculations for the three types of the tetrazole which are 2-(1H-Tetrazole-5-yl)-3-phenylacrylonitrile, 2-(1H-Tetrazole-5-yl)-3-(4-nitrophenylacrylonitrile), and 2-(1H-Tetrazole-5-yl)-3-(4-hydroxyphenyl acrylonitrile) showing the corrosion inhibition efficiency on mild steel in 1M HCl were carried out with the Density Functional Theory (DFT) at the B3LYP functionals with the use of 6-311g (d, p) basis set. Calculated parameters such as E_{HOMO} , E_{LUMO} , energy gap, electronegativity (χ), chemical potential (μ), hardness (η), softness (S), electrophilicity, electrofugality, nucleofugality, Proton affinity, polarizability and hyperpolarizability. The correlation and regression analysis have been conducted to determine which descriptors have effect on inhibition efficiency. Both the theoretical results and experimental data are in accordance based on the inhibition efficiency.

Keywords: Theoretical study, inhibition efficiency, corrosion, DFT

1. INTRODUCTION

Corrosion processes and inhibition studies by organic inhibitors are a very active field of research [1]. Some of the physical-chemical and electronic properties of the organic inhibitor depend on functional groups, steric effects, electron density and donor atomic properties; and these properties have been reported by many researchers to influence the efficiency of the inhibition [2, 3]. The formation of a film that is adsorbed physically and / or chemically to the metal surface by the inhibitor reveals the inhibition mechanism [4]. Heteroatoms containing atoms such as sulfur, nitrogen and

oxygen increase the inhibitor effect of the compounds [5]. The steel material, which is widely used in industrial processes, during industrial cleaning, petrochemical processes is easily abraded in the acid solution [6]. Synthetic inhibitors are widely used to protect metals against corrosion due to their easy and economical synthesis, lower costs and better inhibition efficiency [7]. Most effective inhibitors have been reported to be synthetic compounds containing heteroatoms (such as P, O, S and N) in addition to multiple bonds and all aromatic ring forms [8]. These inhibitors adhere to metal surfaces and form a protective surface film in the metal and also form an electrolyte interface. The adsorption of synthetic inhibitors on the metal surface depends on many factors including the properties of the metal and the inhibitor and the working conditions [9].

In the present study, calculations with Density Functional Theory (DFT) at the B3LYP functionals by using 6-311g (d, p), basis set for three tetrazole derivatives, which are 2-(1H-Tetrazole-5-yl)-3-(4-hydroxyphenyl acrylonitrile) **1**, 2-(1H-Tetrazole-5-yl)-3-(4-nitrophenylacrylonitrile)-2, and 2-(1H-Tetrazole-5-yl)-3-phenylacrylonitrile **3** were performed to determine quantum chemical parameters and to correlate with the experimental inhibition efficiency. Some common theoretical parameters, namely, E_{HOMO} , E_{LUMO} , energy gap, hardness (η), electronegativity (χ), softness (S), chemical potential, electrofugality, nucleofugality, electrophilicity, proton affinity, polarizability and hyperpolarizability dipole moment (DM), Mullikan charges on atoms for the neutral and protonated forms in the water and gas phase. The correlation between the parameters mentioned above and the inhibition efficiency have been discussed in gas and water phases for the protonated and natural forms with the Density Functional Theory (DFT) at the B3LYP functional with 6-311g (d, p), basis set. For three molecules, using regression analysis help determine the key descriptors affecting on inhibition efficiency. With both models having $R^2=0.99$ values, average polarizability has effect on inhibition efficiency.

2. COMPUTATIONAL DETAILS

2.1 Calculation Method

All the calculations were performed with complete geometry optimization by using the standard Gaussian (09) software package with B3LYP [10].]. The calculations of the n tr and protonated form of the molecules under study with the B3LYP functional, which is formed by combining with Becke 1988 exchange functional, correlation function by Lee, Yang and Parr, and 6-311G (d, p) basis set were performed in gas and water phase

2.2. Definitions and Equations

The ability of chemical compounds to electron donating and electron accepting is thought to be related to quantum chemical parameters such as chemical hardness (η), chemical potential (μ) and electronegativity (χ) [11]. Quantum chemical parameters are defined at a constant external potential $v(r)$ as follows, as the derivative of electronic energy (E) according to the number of electron (N).

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

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

From the Eq.1, electronegativity is given as the negative sign of the chemical potential. To calculate approximately electronegativity, chemical potential and the chemical hardness, Pearson and Parr applied the finite differences approach [11] to the mathematical definitions given above and provided the following equations based on ground state ionization energy (I) and ground state electronegativity (A) values of chemical species (atom, ion or molecule) to calculate aforementioned parameters.

The softness which can be expressed as a measure of polarization can be defined by 1 equation

$$\sigma = 1/\eta \quad (3)$$

$$\eta = \frac{I - A}{2} \quad (4)$$

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

According to the Koopmans theorem, the ionization energy and electron affinity are defined as the negative values of the highest occupied molecular orbital energies and lowest molecular orbital energies, respectively ($-E_{HOMO} = I$ and $-E_{LUMO} = A$). In this case, chemical hardness, can be calculated with the equation 6.

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2} \quad (6)$$

Chemical potential and electronegativity can be calculated by using the equation 7.

$$\mu = -\chi = \frac{E_{LUMO} + E_{HOMO}}{2} \quad (7)$$

According to Parr and co-workers [13], global molecular electrophilicity (ω_{mol}) and global molecular nucleophilicity (ε_{mol}) index can be calculated based on molecular electronegativity and molecular hardness values of studied compounds with the help of the following equations, respectively.

$$\omega_{mol} = \frac{\chi^2_{mol}}{2\eta_{mol}} \quad (8)$$

$$\varepsilon_{mol} = 1/\omega_{mol} \quad (9)$$

The second order of change in the energy gives the electric dipole polarization (α) which is defined as a measure of the linear response of the electron density in the presence of an infinite electric field (F). The polarisability (α) is calculated as the average value and is pressed out along the equation 10.

$$\alpha = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (10)$$

Polarization is expressed as inversely proportional to the third force of the hardness values. [14]. Anisotropy of polarization is another important molecular feature of its electronic properties [15]. The anisotropy of the polarizability ($\langle \Delta\alpha \rangle$) was calculated by using the following equation.

$$\langle \Delta\alpha \rangle = \left[\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2)}{2} \right]^{1/2} \quad (11)$$

In aromatic molecules, the contribution to the polarization of the molecules in the vertical direction comes from the polarization of the sigma bonds not from π electrons of the aromatic molecules in a direction perpendicular to the plane. Since the anisotropy j becomes zero for the spherical symmetric charge distribution, it gives a measure of the spherical symmetry deviations and defined as following;

$$\kappa = \frac{(\alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2)}{6 \langle \alpha \rangle^2} \quad (12)$$

The average polarization and κ anisotropy are large experimental interest quantities in the theory of optoelectronic and intermolecular forces. Hyperpolarizability is explained by the calculation of boundary molecular orbital energies that aid in the use of intramolecular charge transfer to account for hyperpolarizability [16]. In this study, the values of the first hyperpolarizability were obtained using the following equations:

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (13)$$

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \quad (14)$$

The proton affinity (PA) for the $A^- + H^+ \rightarrow AH$ reaction is obtained using the following equation and is [15].

$$PA = E_{(\text{pro})} - (E_{(\text{non-pro})} + E_{H^+}) \quad (15)$$

where, E_{H^+} , E_{pro} and $E_{\text{non-pro}}$ and are the energies of H^+ ion, protonated and the non-protonated inhibitors, respectively. E_{H^+} was obtained as:

$$E_{H^+} = E_{(H_3O^+)} - E_{(H_2O)} \quad (16)$$

In chemical reactions, proton affinity, that is an important parameter, plays a key rule in the understanding of enzyme reaction, acid-base reactions, electrophilic addition and adduct reaction

The proton affinity, which is an important parameter in chemical reactions, [17] plays an important role in the understanding of enzyme reaction, electrophilic addition, acid-base reactions.

Gas phase proton affinities (PA) can be measured by various experimental techniques. However, the area of the preferred protonation of a particular species cannot be experimentally obtained and theoretical calculations to obtain the information must be applied. Theoretical calculations should be performed to get knowledge the preferred protonation site in a given molecule, since this knowledge could not be obtained experimentally. Quantum chemical calculations give

information complementing the experimental data like protonation sites, energies and structures of the molecules [18].

3. STATISTICAL ANALYSIS

there are Three different molecules with non-protonated phases denoted by **1-2p**, **2-2p** and **3-2p** using the values of twenty-one quantum descriptor variables, namely, E_{HOMO} , E_{LUMO} , I , A , Energy Gap, Dipole Moment, Mulliken Atomic, Hardness, Softness, Electronegativity, Chemical Potential, Global Electrophilicity Index, Global Molecular Nucleophilicity, SEZPE, Nucleofugality, Electrofugality, Anisotropy, Average Polarizability, K_{p} , P_{z} and PA are called independent variables. The Inhibition Efficiencies (IEs) of those molecules are dependent variable. In this study, we try to examine the relationship between those descriptors and IE using linear regression. The data is extracted using the method called B3LYP-6-311-g(d,p). Since independent variables, namely, quantum descriptors highly are correlated, our models boil down to a two-descriptor model after eliminating highly correlated ones in regression analysis using back-ward elimination, which results in a model given in (17) having high determination of coefficient 0.99.

The model is given as follows:

$$IE = 57.870 + 0.113 * \textit{average polarizability} - 0.026 * PA \quad (17)$$

On the other hand, the same steps are taken towards analyzing relationship using same variables under the different phases denoted by **1-2p-w**, **2-2p-w** and **3-2p-w** respectively. The model with $R^2=0.99$ is given as follows:

$$IE = 57,351 + 0.114 * \textit{avaerage polarizability} - 0.104 * PA \quad (18)$$

4. RESULTS AND DISCUSSION

They were performed the corrosion inhibition efficiency for the compounds **1**, **2** and **3** on mild steel in 1 M HCl and reported that the $\eta\%$ of the tetrazole series under study with the concentration 40 (mg /l) having the order **1** (98.96%) > **2** (96.9 %) > **3** (93.99 %) [20]. The Inhibition results were compared with the theoretical calculations. Optimized geometries, the HOMO, the LUMO and the total electron density of each compound for the neutral molecules under study in gas phase are given in Figure 1. As seen from the Figure 1. HOMO is composed of the whole molecule the compounds **1**, **2** and **3**

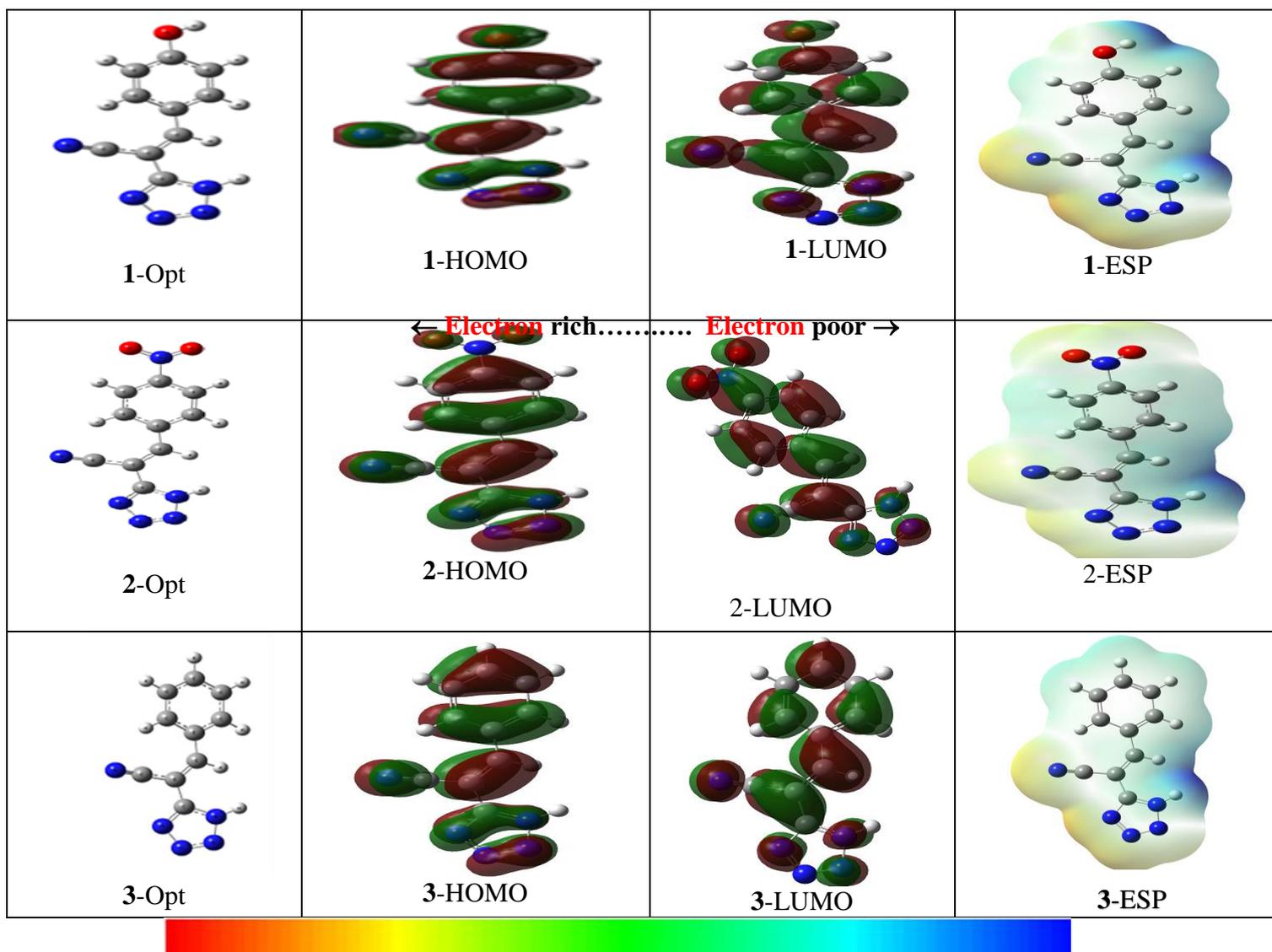


Figure 1. The optimized molecular structure HOMO, LUMO and the total electron density for the compounds **1**, **2** and **3**

The proton affinities, gas phase dependence, ionization energies and electron affinity of the molecules in the equilibrium are found by calculations on protonated molecules. The presence of different reactive sites in the studied inhibitors results from free electrons in the tetrazole ring on the nitrogen atoms, suggesting that there is a large tendency to protonate in the acidic medium and consequently a high likelihood of reaction as a cationic inhibitor on the surface metal. Ionisation and proton transfer reactions are important parameters that play an important role in chemistry and biochemistry. They are used in order to predict the inhibitory yield of chemical compounds [21].

We calculated proton affinity of the studied molecules considering the following formulas

$$PA = E_{(\text{pro})} - (E_{(\text{non-pro})} + E_{H^+}) \quad (17)$$

Where, $E_{non-pro}$ and E_{pro} are the energies of the non-protonated and protonated inhibitors, respectively. E_{H^+} is the energy of H^+ ion. The most stable structure given in Table 1 is the one associated with the lowest values of proton affinity (PA).

Table 1. Proton affinity Energies for Tetrazole in gas and water

compunds	PA (kJ mol ⁻¹)	
	Gas Phase	Water Phase
1 -2p	-221.482	-79.238
1 -3p	-192.436	-60.683
1 -4p	-136.271	-24.365
2 -2p	-169.783	-60.400
2 -3p	-88.424	-9.980
2 -4p	-88.424	-9.977
3 -2p	-202.439	-70.783
3 -3p	-177.426	-55.837
3 -4p	-118.478	-17.725

When examining the correlation between molecular structure and corrosion inhibition yield, using the quantum chemical calculations is very important.. The Quantum chemical calculations and molecular modeling methods are widely used to characterize the molecules in terms of reactivity shape and binding properties [22].

The higher the E_{HOMO} value is the stronger the electron donating capability of the inhibitor will be better to observed inhibition efficiency [23]. The LUMO implies the ability of molecules to accept electrons from the metallic surface. The lower the value of E_{LUMO} , the more susceptible it is to accept electrons [24].

Frontier Orbital Energies calculated with B3LYP/6-311g (d,p) basis set the compounds **1**, **2** and **3** in four situations (Neutral form of gas and water phase, protonated form in gas and water) were given in Figure 2. The frontier molecular orbital graph consisting of five molecular orbitals near HOMO and five molecular orbitals near LUMO, for the neutral and protonated molecules are shown in the graph and Table 2,3, and 4 the compounds **1**, **2** and **3**, respectively.

The analysis of electronic properties of the protonated species reveals a change in chemical properties such as the electron donating capability of the inhibitors to the metal. The energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$), decreases/increases with an increase in the number of protons for protonation. The E_{LUMO} of these molecules values calculated for three compounds study with the three different situations (no protonated, protonated, and protonated-water phase). The energies of the HOMO for the protonated molecules in the gas phase are lower than those of the nonprotonated molecules in gas phase where species were -7.12 eV, -6.467 eV, and -7.037 eV.

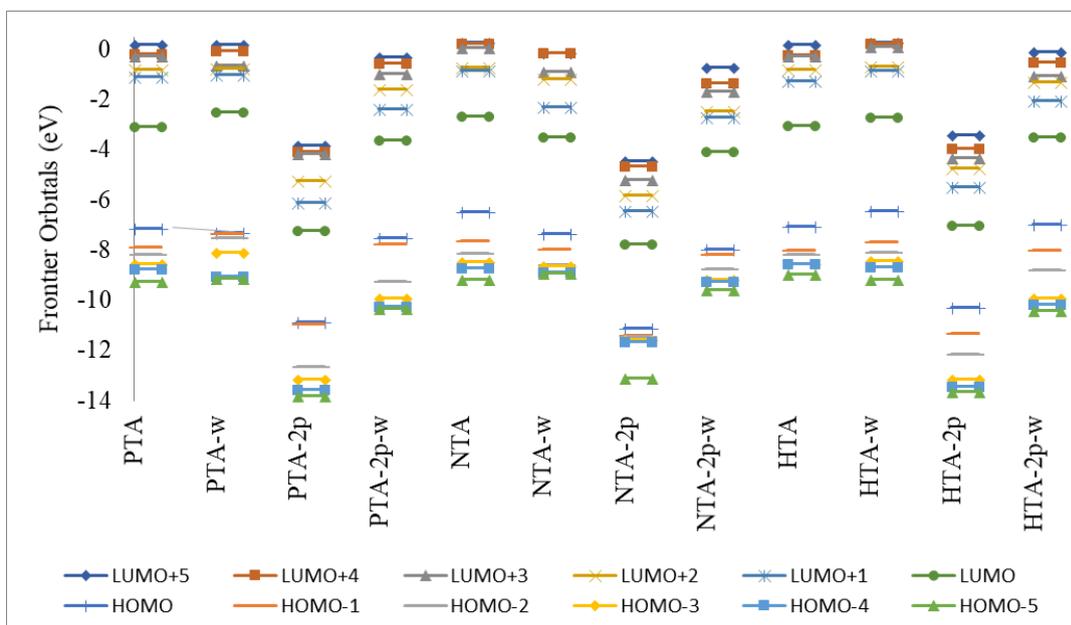


Figure 2. Frontier Orbital Energies Calculated with B3LYP/6-311g(d,p) for the compounds **1**, **2** and **3** for the four situation (Neutral form in gas and water phase, protonated form in gas and water phases).

From Table 6, it can be concluded that the electron donating ability follows the following order: **3** > **2** > **1**. The lowest unoccupied molecular orbital (MO) energy indicates the tendency of molecules to accept electrons. The lower value of E_{LUMO} shows that molecules become stronger when they accept electrons.

The gap energy between the lowest unoccupied MO energy and the highest occupied MO energy is expressed to be great important in the definition of static molecular reactivity. The larger the energy gap, the lower the stability and reactivity of the molecule.

Indeed, the large values of the energy vacancy (ΔE) signify high electronic stability and low reactivity, a low energy range implies higher inhibitor yields when describing static molecular reactivity [25].

ΔE values for the compounds **1**, **2** and **3** are 4.0 eV, 3.804 eV 4.07 eV (Table 2-4) As seen from the results ΔE values do not appear to be a definitive description of the reactivity of the corrosion inhibitors studied. However, in the solvent phase calculations seems ΔE values appear to be a definitive explanation of the reactivity of the corrosion inhibitors studied. Calculations appear in the solvent phase. ΔE values for the compounds **1**, **2** and **3** are 3.744 eV, 3.824 eV 4.80 eV

Quantum chemical parameters like ionization energy, electron affinity, electronegativity (χ), chemical potential (μ), highest occupied MO energy (E_{HOMO}) and lowest unoccupied MO energy (E_{LUMO}), the energy gap (ΔE), dipole moment (DM), Global electrophilicity index (ω), global molecular nucleophilicity (ϵ), Mullikan Atomic (TNC), nucleofugality, electrofugality, polarizability, hyperpolarizability, global softness (S) and absolute hardness (η). The highest occupied MO (E_{HOMO}) and the lowest unoccupied MO (E_{LUMO}) are very useful for illuminating the chemical reactivity of a molecule and provide important clues to theoretically predict the inhibition yield of molecules. [26].

Table 2. The calculated some parameters of compound **1** for using B3LYP-6-311g (d,p) method.

Parameters	1	1-2p	1-2p-w	1-3p	1-3p-w	1-4p	1-4p-w	1-w
E_{HOMO} (eV)	-7.0369	-10.288	-6.9667	-9.8596	-6.7904	-9.9984	-6.8429	-6.4320
E_{LUMO} (eV)	-3.0371	-6.9991	-3.4981	-6.8712	-3.3144	-7.0998	-3.5511	-2.6874
I	7.0369	10.2884	6.9667	9.8596	6.7904	9.9984	6.8429	6.4320
A	3.0371	6.9991	3.4981	6.8712	3.3144	7.0998	3.5511	2.6874
ΔE (eV)	3.9998	3.2893	3.4687	2.9884	3.4760	2.8986	3.2918	3.7446
DM	10.6341	5.2763	7.5122	9.4042	14.1248	12.0437	17.1292	14.7578
TNC	-1.7168	-1.5179	-1.6517	-1.4456	-1.6556	-1.3915	-1.6428	-1.9742
η	1.9999	1.6447	1.7343	1.4942	1.7380	1.4493	1.6459	1.8723
σ	0.5000	0.6080	0.5766	0.6693	0.5754	0.6900	0.6076	0.5341
χ	5.0370	8.6438	5.2324	8.3654	5.0524	8.5491	5.1970	4.5597
μ	-5.0370	-8.6438	-5.2324	-8.3654	-5.0524	-8.5491	-5.1970	-4.5597
ω	6.3431	22.7142	7.8929	23.4173	7.3436	25.2146	8.2049	5.5523
ε	0.1577	0.0440	0.1267	0.0427	0.1362	0.0397	0.1219	0.1801
SEZPE	-1.717	-1.518	-1.652	-1.446	-1.656	-1.391	-1.643	-1.974
Nucleofugality	2.306	14.893	3.528	15.799	3.160	17.390	3.831	1.929
Electrofugality	12.380	32.180	13.992	32.530	13.265	34.488	14.225	11.048
Anisotropy (k)	43.3561	62.3743	54.6863	61.5478	51.0493	70.6415	54.9139	45.9360
Averg. polarizability	269.235	309.544	290.898	311.501	283.956	333.123	294.381	272.775
Pz (Phenyl elect density)	-0.018	0.168	0.124	0.135	0.081	0.162	0.101	0.018
kappa	0.126	0.204	0.177	0.196	0.161	0.227	0.176	0.139
PA (k. joule/mole)		-221.48	-79.24	-192.4	-60.68	-136.27	-24.36	

In the protonated gas phase the values of E_{HOMO} for the compounds **1**, **2** and **3** (-10.288 eV, -11.111 eV -10.87 eV are 4.0 eV, 3.804 eV 4.07 eV are lower than those in nonprotonated compounds, (-7.0369 eV, -6.467 eV and -7.12 eV. Also, in the protonated water phase the values for the E_{HOMO} in the molecules 1-2p-w, 2-2p-w and 3-2p-w (6.966 eV, -7.958 eV, -7.52 eV) are lower than nonprotonated water phase (-6.432eV eV-7.30 eV, -7.325eV). These results are an indication that protonation reduces the ability of inhibitors to give electrons. However, the energy of the LUMO is lower in the protonated gas than that in the no protonated gas phase indicating that there is an increase in electron accepting ability of the inhibitors from the d-orbital of the metal. A low energy gap, coupled with structural stabilities, should favor the adsorption of protonated species on a metallic surface. A large amount of the protonated species will be adsorbed to the metallic surface. Also, the higher concentrations and toward equilibrium, desorption of the protonated species will be rapid from the metallic surface due to charge repulsion and molecular distortion of the molecules from planarity thereby facilitates the adsorption of neutral species at equilibrium metallic surface.

Table 3. The calculated some parameters of compound **2** for using B3LYP-6-311g (d,p) method.

Parameters	2	2-2p	2-2p-w	2-3p	2-3p-w	2-4p	2-4p-w	2-w
E_{HOMO} (eV)	-6.467	-11.111	-7.958	-10.940	-7.874	-10.940	-7.874	-7.325
E_{LUMO} (eV)	-2.663	-7.751	-4.078	-7.879	-4.067	-7.879	-4.067	-3.500
I	6.467	11.111	7.958	10.940	7.874	10.940	7.874	7.325
A	2.663	7.751	4.078	7.879	4.067	7.879	4.067	3.500
ΔE (eV)	3.804	3.360	3.880	3.061	3.807	3.061	3.807	3.825
DM	5.145	10.993	15.849	18.264	23.575	18.264	23.415	8.292

TNC	-1.576	-1.488	-1.654	-1.390	-1.627	-1.390	-1.627	-1.902
η	1.902	1.680	1.940	1.531	1.903	1.531	1.903	1.912
σ	0.5258	0.5953	0.5155	0.6533	0.5254	0.6533	0.5254	0.5229
χ	4.565	9.431	6.018	9.409	5.971	9.409	5.971	5.412
μ	-4.565	-9.431	-6.018	-9.409	-5.971	-9.409	-5.971	-5.412
ω	5.479	26.475	9.334	28.920	9.365	28.920	9.365	7.659
ε	0.1825	0.0378	0.1071	0.0346	0.1068	0.0346	0.1068	0.1306
SEZPE	-1.576	-1.488	-1.654	-1.390	-1.627	-1.390	-1.627	-1.902
Nucleofugality	1.865	17.884	4.286	20.276	4.346	20.276	4.346	3.203
Electrofugality	10.996	36.7458	16.3218	39.095	16.2871	39.0948	16.2871	14.0274
Anisotropy (k)	44.252	50.591	46.497	53.690	46.267	53.690	46.270	46.272
Averg. polarizability	290.129	303.040	289.702	315.104	290.933	315.104	290.944	291.415
Pz (Phenyl elect density)	0.1055	0.2536	0.2068	0.2434	0.1911	0.2434	0.1912	0.1430
kappa	0.1139	0.1377	0.1267	0.1465	0.1260	0.1465	0.1260	0.1234
PA (k. joule\mole)		-169.783	-60.3996	-88.42	-9.980	-88.43	-9.977	

Table 4. The calculated some parameters of compound **3** for using B3LYP-6-311g (d,p) method.

Parameters	3	3-2p	3-2p-w	3-3p	3-3p-w	3-4p	3-4p-w	3-w
E_{HOMO} (eV)	-7.12	-10.87	-7.52	-10.47	-7.34	-10.58	-7.44	-7.30
E_{LUMO} (eV)	-3.05	-7.23	-3.61	-7.16	-3.48	-7.47	-3.71	-2.50
I	7.124	10.865	7.520	10.472	7.338	10.575	7.436	7.300
A	3.054	7.230	3.607	7.158	3.484	7.473	3.709	2.50
ΔE (eV)	4.070	3.635	3.913	3.314	3.855	3.103	3.727	4.80
DM	7.996	3.914	5.860	8.529	12.643	10.918	15.474	10.601
TNC	-1.145	-1.197	-1.340	-1.145	-1.322	-1.095	-1.311	-1.605
η	2.035	1.818	1.957	1.657	1.927	1.551	1.863	2.40
σ	0.491	0.550	0.511	0.603	0.519	0.645	0.537	0.417
χ	-5.089	-9.048	-5.563	-8.815	-5.411	-9.024	-5.573	-4.900
μ	5.089	9.048	5.563	8.815	5.411	9.024	5.573	4.900
ω	6.363	22.519	7.909	23.445	7.596	26.245	8.333	5.003
ε	0.1572	0.0444	0.1264	0.0427	0.1317	0.0381	0.1200	0.1999
SEZPE	-1.4147	-1.1967	-1.3400	-1.1446	-1.3222	-1.0951	-1.3106	-1.6053
Nucleofugality	2.2915	14.3801	3.3242	15.4592	3.1484	17.9972	3.6919	1.3024
Electrofugality	12.4695	32.4756	14.4505	33.0887	13.9702	36.0451	14.8369	11.1024
Anisotropy (k)	37.1021	47.5909	42.0753	46.5307	40.0893	52.0036	41.7283	38.3262
Averg. polarizability	249.7297	272.4073	257.3200	272.4417	252.9660	287.4183	258.7650	249.6210
Pz (Phenyl elect density)	0.0865	0.2819	0.2287	0.2462	0.1768	0.2712	0.1929	0.1194
kappa	0.1068	0.1515	0.1316	0.1452	0.1230	0.1655	0.1300	0.1142
PA (k. joule\mole)		-202.439	-70.783	-177.43	-55.837	-188.48	-17.725	

Another very important electronic parameter that originates from the uneven distribution of the loads on the various atoms of the molecule is the dipole momentum. The adsorption, between the chemical compound and the metal surface, increases with increasing dipole moment [26]. The high

dipole moment in the molecules probably increases the adsorption on the metal surface [27]. In this study, the dipole moment values seem to support this perspective. The DM for the compound **1** in the gas phase has the highest value of the others (Figure 3).

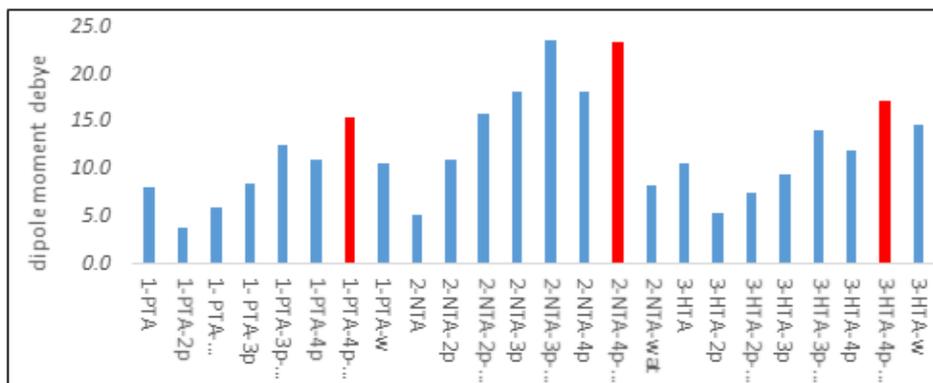


Figure 3. DM calculated with B3LYP/6-311g(d,p) for the compound **1**, **2** and **3** for the four situation (neutral form in gas and water phase, protonated form in gas and water phase).

Since the compound with a large MV value has the highest surface coverage, inhibitors with large molecular bulk can provide a very large protection to the metal surface. This is supported by the fact that the MV values are in the range of $1 > 2 > 3$. This order in the MV values is in agreement with the experimentally determined inhibition efficiency [28].

A sign of the molecular capacity of the electron donation is the total negative charge (TNC). The TNC values of compounds **1**, **2** and **3** given in Tables 2-4 shows that compound **1** strongly adsorbs to the mild steel surface compared to the compounds **2** and **3**.

Chemical Hardness (η) is a measure of the ability of atom or molecule to transfer the charge. Increasing (η) decreases the stability of molecule [29]. It is calculated by using equation 7 [30]. Compound possessing a high value of (η) is considered to be a good inhibitor. (η) Values for molecule **3** in gas and water phase for neutral and protonated form is 2.40eV, 2.035 eV, 1.818 eV and 1.863 eV shown in Table 2, 3 and 4.

Chemical Softness (S), a measure of the flexibility of an atom to receive electrons (S), was calculated by using equation 5. Molecules having a high value of S are considered to be a good inhibitor. The values of S in the gas with proton is (0.645eV), the decrease in both gas phase and water solvents to (0.4491eV), Table 2, 3 and 4.

Global electrophilicity index, (ω), is the measure of the stability of an atom after gaining an electron, Lower value of (ω) meaning the molecule has a good inhibition. It is calculated by using equation 10. The values of ω for the compounds **1**, **2** and **3** are shown in Table 2-4. (In the gas phase they are 6.3431, 5.479 and 6.363, in water 5.5523, 7.659 and 5.003, respectively).

Since polarization has an important role in preventing corrosion, the higher the degree of polarization, the easier and stronger the adsorption of the inhibitor to the metal surface. The adsorption of the inhibitors on the metal surface is so easy that the higher the value of the polarization.

The polarizability values for compounds **1**, **2**, and **3**, calculated using Equation 12, are given in Table 2-4. As can be seen from the Table 2-4, the polarizability order of the molecules is in the form of **1** > **2** > **3** supports that if the polarization values of the inhibitors are high, the inhibition efficiency is high.

Table 5. Calculated % R² of the compounds **1**, **2** and **3** for the quantum chemical parameters versus inhibition efficiencies.

quantum chemical parameters for the Tetrazole molecules	Neutral		Protonated	
	% R ²			
	Gas phase	Water phase	Gas phase	Water phase
E _{HOMO} (eV)	3.42	67.0	40.36	60.95
E _{LUMO} (eV)	1.04		5.68	80.49
Energy gap (eV)	9.95	85.43	93.06	76.57
Dipole Moment	17.95	63.87	5.94	4.71
Mulliken Atomic TNC (e)	99.94	92.69	86.52	79.89
hardness (η)	71.93	85.43	93.06	76.57
Softness (S)	66.35	86.69	93.91	68.97
Electronegativity (eV)	2.4		20.91	15.28
chemical potential (eV)	2.35		20.91	15.28
Global electrophilicity index(ω)	0.7		1.15	62.09
Global molecular nucleophilicity	0.65		1.32	75.29
SEZPE (eV)	99.94	92.69	86.52	79.87
Nucleofugality (eV)	1.38		99.98	64.81
Electrofugality (eV)	0.12		39.3	64.81
anisotropy (k)	28.9	77.25	85.25	94.6
Polarizability	70.41		88.49	82.74
Kappa	95.33	95.59	49.94	60.73
p _z for the (Phenyl elect density)	48.88	51.85	88.49	85.79
Hyperpolarizability	54.94	99.53	97.1	35.91

Phenyl p_z electrons are delocalized in molecular orbitals, extending around the ring, above and below the plane of the ring

In general, the electron is more likely to be found in regions with high electron density. The P_z values for the phenyl electron density of the tetrazole derivatives. Electrons of the more electronegative atom will have a greater contribution to the formation of a bond. Charge density of phenyl group for the compound **1** being -0.018 e̅ reflect this greater electron density. Less electronegative phenyl groups will have a partial positive charge that reflects the lack of electron density.

5. CONCLUSIONS

In the present study, the frontier molecular orbital pictures of the neutral and protonated compounds **1**, **2** and **3** were studied in gas and water phase. The calculated parameters namely the energy of the highest occupied MO, the energy of the lowest unoccupied MO, their energy gap (E_{HOMO}–E_{LUMO}), MD, softness, hardness were called independent variables to determine inhibition efficiency in modeling endeavor. It may be observed that most of the quantum chemical parameters for

the protonated forms of the tetrazoles are in accordance with the quantum chemical parameters obtained from the neutral forms.

In this Theoretical study, we calculated the HOMO and LUMO orbital energies by using B3LYP method with 6-311g (d,p). All other calculations were performed using the results with some assumptions. The higher values of E_{HOMO} indicate an increase for the electron donor and this means a better inhibitory activity with increasing adsorption of the inhibitor on a metal surface, whereas E_{LUMO} indicates the ability to accept electron of the molecule. The adsorption ability of the inhibitor to the metal surface increases with increasing of E_{HOMO} and decreasing of E_{LUMO} .

The values of polarizability were obtained with B3LYP/6-311g (d, p) method for compounds **1**, **2**, **3**, and molecules for four situations (Neutral form of gas and water phase, protonated form in gas and water). The results obtained for polarizability are bigger values which means that greater the possibility of molecule to change its original shape and better tendency, the molecule will have to be absorbed on the metal surface. In the case of molecules study for the compounds **1**, **2**, **3** the order is for the protonated form is $1 > 2 > 3$ in accordance with the quantum chemical parameters obtained from the neutral forms.

Keeping in mind that the results are obtained with very limited number of datasets for the statistical analysis, there exist two different models for the inhibition efficiency (%IE). The first model is based on descriptor variables of three molecules, namely, **1-2p**, **2-2p** and **3-2p** respectively. Except the constant term, the first model consists of two descriptors such as average polarizability and proton affinities. It should be noticed that although average polarizability has impact positively on IE, the proton affinities plays the decreasing role on it.

The second model consisting of the same variables just as the first model represent the molecules namely, **1-2p-w**, **2-2p-w** and **3-2p-w**. It should be noticed that although average polarizability has impact positively on the inhibition efficiency (%IE), the Proton affinities (PA) decreases in the inhibition efficiency (%IE). Both models have same determination of coefficient of 0.99.

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