

Theoretical Studies on the Corrosion Inhibition Characteristics of Thiosemicarbazide Derivatives

Abdelhakim Alrjaibi¹, Murat Saracoglu², Mohammed A. Amin³, Emel Bayol⁴, Fatma Kandemirli⁵

¹Materials Science and Engineering Dept., Faculty of Engineering and Architecture, Kastamonu Univ., 37200 Kastamonu, Turkey

²Faculty of Education, Erciyes University, 38039 Kayseri, Turkey

³Materials and Corrosion Lab (MCL), Dept. of Chemistry, Faculty of Science, Taif University, 888 Hawaiya, Taif, Saudia Arabia

³Department of Chemistry, Faculty of Science, Ain Shams University, 11566 Abbassia, Cairo, Egypt

⁴Department of Chemistry, Faculty of Art and Science, Niğde Ömer Halisdemir University, 51240 Niğde, Turkey

⁵Biomedical Engineering Dept., Faculty of Engineering and Architecture, Kastamonu University, 37200 Kastamonu, Turkey

(²muratsaracoglu@gmail.com)

Abstract- Quantum chemical calculations using B3LYP and RHF methods with the 6-311G(d,p) and 6-311++G(2d,2p) basic sets and CBS-Q method were used and performed to give further insight into the inhibition mechanism of benzaldehyde thiosemicarbazone (BTSC), p-chlorobenzaldehyde thiosemicarbazide (PCIBTSC), 4-dimethylaminobenzaldehyde thiosemicarbazide (4DMBTSC) for neutral and protonated forms in gas phase and water phase. These include, energy of the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap between E_{LUMO} and E_{HOMO} (ΔE), chemical hardness (η), softness (σ), electronegativity (χ), chemical potential (μ), global electrophilicity (ω), nucleofugality (ΔE_{n}) and electrofugality (ΔE_{e}) were found correlation coefficient between the experimental inhibition efficiency (IE%) and theoretical results.

Keywords- Corrosion, Inhibitors, Thiosemicarbazone; Theoretical Studies

I. INTRODUCTION

It is important to use various methods to prevent and control corrosion of the industrial application materials. For this purpose, to be achieved properly, organic compounds having π bonds and hetero-atoms, such oxygen (O); nitrogen (N) and sulfur (S), have been widely used.[1-3] In general, the inhibitor molecule may be physically or chemically adsorbed on the corrosive metal surface (CMS). A layer (or film) of the adsorbed molecules is subsequently formed on the CMS serving as a barrier against corrosion.[4,5] It is widely recognized that organic inhibitors typically promote the formation of chelates on the metal surface, by transferring electrons from the organic compound to the metal. This in turn forms a coordination covalent bond during chemical adsorption.[6,7] Factors that influence the adsorption of these molecules, such as functional groups, space factors, molecular size, electron density on donor atoms, and orbital characteristics of donor electrons have been considered and discussed.[8-18] The efficiency of an organic inhibitor is closely related to its adsorption capability, which in turn depends on the molecular properties of the different species included in it.[18-20]

The use of theoretical chemistry recently to explain the mechanism of corrosion inhibition, such as quantum chemistry calculations, has proved to be a very powerful tool for studying the mechanism.[18,20-22] Previous study has been successful in quantum chemistry studies to corrode the effectiveness of certain types of organic compounds with molecular orbital (MO) inhibition (eg amino acids, amides,[23,24] and hydroxycarboxylic acid pyridopyrazoles[25]) horizontal related compounds are associated with compounds sulphonamides.[26] There are many applications in using the HOMO-LUMO gap as a quantum descriptor for establishing correlations in various chemical and biochemical systems.[23] Quantum chemical descriptors such as chemical potential, chemical hardness, softness, electrophilic index and Fukii function have been widely used to explain the mechanism of corrosion inhibition.[27-29] Quantum chemical calculations have been widely used in the study of reaction mechanisms.[30] Recent studies have shown that quantitative chemical calculations are important as a major tool studied for the mechanism of inhibition.[28,31-33] Therefore, in order to understand the adsorption of the inhibitor at the metal-solution interface, it is necessary to understand the influence of all factors as much as possible. Recently, high molecular weight organic substances, especially surfactants, have been used as preservatives for copper alloys.[34,35] Surfactants can significantly alter the interfacial properties; therefore, they are also used in many industrial processes such as dispersion flocculation, flotation emulsification and cosmetics.[36-38] It is reported that thiosemicarbazides and their derivatives are potential inhibitors of iron and steel.[39,40] Previous studies on the inhibition of phosphoric acid corrosion by the thiosemicarbazide in the laboratory have shown its value as a corrosion inhibitor.[41] Literature review shows that thiosemicarbazide and its derivative is a potential inhibitor of iron.[39,40] Previous studies have shown that thiosemicarbazide corrosion laboratories inhibit and its valuable sulphate used as an anticoagulant. Mild steel corrosion was assessed to determine the effectiveness of removal of organic compounds, molecular structure and substitutes on interest for benzene ring.[41]

Quantum chemical calculations using different three methods, Hartree-Fock (HF), Møller-Plesset (MP) and density functional theory (DFT/B3LYP) method with SDD, 6-31G(d,p) and 6-31++G(d,p) basis sets were performed some benzaldehyde thiosemicarbazones and their thiole tautomers for three molecules.[42] Quantum chemical calculations using RHF and B3LYP methods with the 6-311G(d,p) and 6-311++G(2d,2p) basic sets and CBS-Q method were used to

establish the correlation between inhibition efficiency and the study of the electronic properties of molecules. The aim of the present work is to investigate the effects of how the relationship changes between structure and activity according to the basis sets and parameters and protonated sites. Theoretical studies on the electronic and molecular structures for investigated molecules, BTSC (1), PCIBTSC (2), 4DMBTSC (3) are given as (Fig.1).[41]

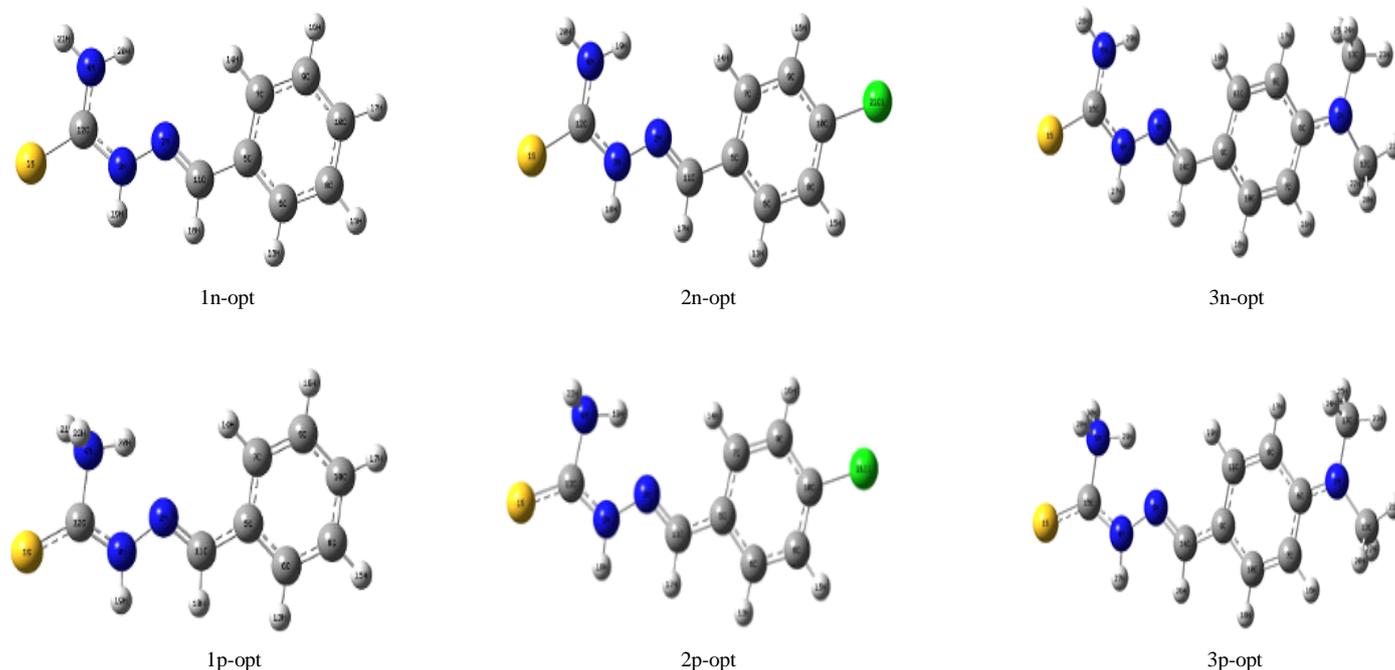


Figure 1. The optimisation form of molecules under study (n: non-protonated (neutral) and p: protonated)

As an inhibitor this study was used to protect the corrosion behaviour's to determine the relationship between the quantum chemical descriptor parameter obtained from the molecular structure of the compound and the inhibition efficiency of the compound treated with standard Gaussian 09 software package.⁴³ Quantum chemical calculations using RHF and B3LYP methods with the 6-311G (d,p) and 6-311++G(2d,2p) basic sets and CBS-Q method were performed.

II. MATERIAL AND METHODS

In this study, density functional theory (DFT) was used. Consider the appropriate theoretical level of electronic structure calculations. It is important to describe the combination of the basics and the method of the system of interest. As an inhibitor, this study was used to protect the corrosion behaviour to determine the relationship between the quantum chemical descriptor parameters obtained from the molecular structure of the compound and the inhibitory efficiency of the compounds treated with the standard Gaussian 09 software package.⁴³ B3LYP and RHF with the basis sets 6-311G (d,p) and 6-311++G(2d,2p), and CBS-Q method were used.

A. Definitions and equations

Quantum chemical parameters such as chemical hardness (η), chemical potential (μ) and electronegativity (χ) like can be measured as electrons or acceptability of compounds. In the conceptual density functional theory (CDFT), which provides an important contribution to the development of quantum chemistry. The above quantum chemical parameters are described as the derivative $\nu(r)$ of the derivative of the electron energy (E) relative to the external constant number of electrons (N).

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (1)$$

Where ΔE its energy gap

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{\nu(r)} \quad (2)$$

$$\eta = \frac{1}{2} \left(\frac{\partial \mu}{\partial N}\right)_{\nu(r)} = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(r)} \quad (3)$$

From the equation; we can see that the electronegativity is given as a negative value of the chemical potential. In order to calculate the chemical hardness, chemical potential and electronegativity, Parr and Pearson[44] apply the finite difference method to the above mathematical definition and based on the ground state ionization energy (I) and the ground state electronegativity (A) chemical value species (atoms, ions or molecules) to calculate the above parameters. Here, it is important to note that the softness (σ) of the polarizability measurement is considered to be the reciprocal of the multiplier of the chemical hardness ($\sigma = 1/\eta$).

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

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

Where (I) and (A) are related to $I = -E_{HOMO}$, $A = -E_{LUMO}$

The ionization energy (I) and the electron affinity (A) of the molecule can be calculated with the help of the Koopmans theorem. According to the theorem, the negative values of the highest occupied and lowest unoccupied molecular orbital energies correspond to ionization energy and electron affinity, respectively. In this case, within the theoretical framework, chemical hardness, chemical potential and electronegativity can be calculated by means of the following equation.

$$\mu = -\chi \cong \frac{E_{HOMO} + E_{LUMO}}{2} \quad (6)$$

$$\eta \cong -\frac{1}{2}(E_{HOMO} - E_{LUMO}) \quad (7)$$

It is well known that the most suitable acid-base definition is defined by the Lewis acid-base. The Lewis acid-base definition, describes the base as an electron donor. It should be noted that there is a significant correlation between alkaline and proton affinity. Proton affinity is also an important parameter used to predict the inhibitory efficiency of the

compound. The nucleofugality (ΔE_n) is related to a molecular fragment's ability to accept an electron, a small value for ΔE_n will be associated with a high nucleofugality. Unlike the ΔE_n , ΔE_e measures the energy required to donate an electron to a perfect electron donor.[45] Nucleofugality (ΔE_n) and electrofugality (ΔE_e) can be calculated by means of the following equations from the chemical hardness (η) and chemical potential (μ).

$$\Delta E_n = \frac{(\mu + \eta)^2}{2\eta} \quad (8)$$

$$\Delta E_e = \frac{(\mu - \eta)^2}{2\eta} \quad (9)$$

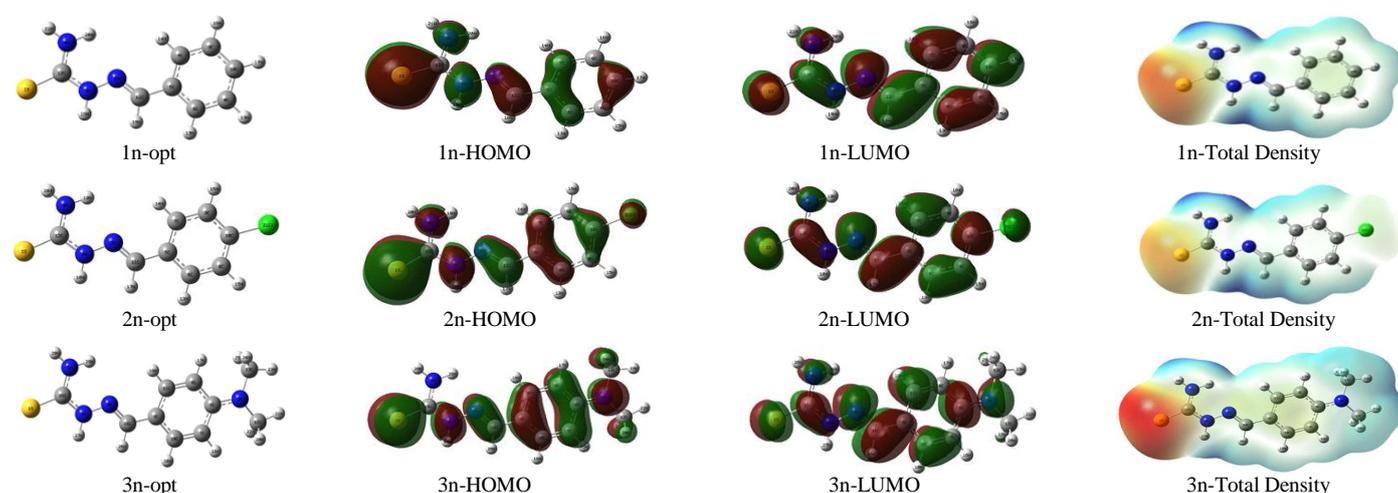
According to Parr and colleagues, [44] Global electrophilicity index (ω) index can be calculated according to the following equation to study the molecular electronegativity and molecular hardness values of the compounds

$$\omega = \frac{\chi^2}{2\eta} \quad (10)$$

III. RESULTS AND DISCUSSION

This study was used to determine the relationship between the quantum chemical descriptor parameters obtained from the molecular structure of the compound and the inhibitory efficiency of the compounds treated with the standard Gaussian 09 software.[43] Three molecules, for the non-protonated and protonated for gas and water phase compounds were used for this purpose (see Fig. 1). In this study, nucleofugality (ΔE_n) and electrofugality (ΔE_e) have been calculated with a detailed quantum chemical study.

The most important orbital in the molecule is the so-called frontier orbitals known as HOMO and LUMO. LUMO the lowest unoccupied molecular orbital HOMO is the highest energy MO (Fig. 2).



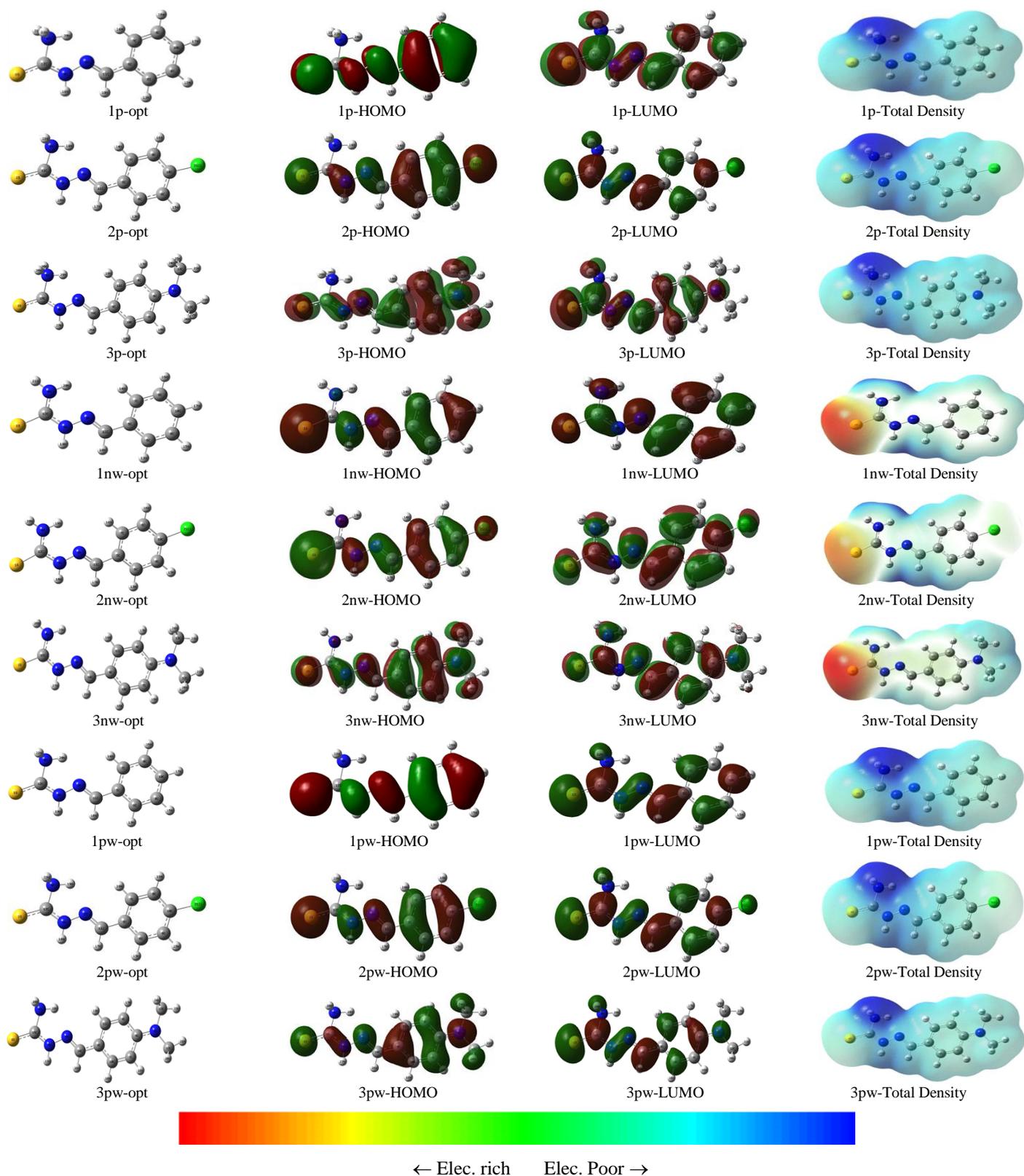


Figure 2. The optimized molecular structures, HOMOs, LUMOs and total density of the non-protonated and protonated forms in gas and in the presence of water phase inhibitor molecules using DFT/B3LYP/6-311++G(2d,2p); (n: non-protonated (neutral), nw: non-protonated in the presence of water, p: protonated, pw: protonated with in the presence of water)

The electron density of the HOMO location in the BTSC, PCIBTSC, 4DMBTSC inhibitors is mostly distributed on the phenyl and thiosemicarbazide groups indicating that these are the favourite adsorption sites. The HOMO and LUMO population of molecules for all calculations can be seen in Fig. 2. Also, we see molecular electrostatic map (total density) of the investigated molecules at B3LYP/6-311++G(2d,2p) method of the non-protonated and protonated forms in gas and in the presence of water phase inhibitor molecules using DFT/B3LYP/6-311++G(2d,2p). It is seen that the electron density for 1, 2 and 3 molecules are high in sulphur atoms for non-protonated and non-protonated in the presence of water phase. The highest electron density is seen in the sulphur atom at molecule 3 and the least electron density at molecule 2 for non-protonated and non-protonated in the presence of water phase. The order of electron density of the three investigated species for non-protonated and non-protonated in the presence of water phase is 4DMBTSC (3) > BTSC (1) > PCIBTSC (2) as compatible with the experiment inhibition efficiency results. This proves that the -N(CH₃)₂ substituent is a group capable of strong resonance electron donation to the phenyl ring. In this group the electron distribution is uniform throughout the structure. The electron density is reduced at nitrogen atoms for protonated and protonated in presence of water molecules (Fig. 2).

Chemical hardness, softness and HOMO-LUMO energy gap are closely related to the chemical properties. The chemical hardness introduced by Pearson in the 1960s is defined as the resistance of electron cloud polarization or chemical deformation. The maximum hardness principle states that the chemical system tends to arrange itself to obtain maximum hardness and chemical hardness can be considered a measure of stability. Pearson shows that the hard molecules with high HOMO-LUMO energy gap values more stable molecules with low HOMO-LUMO energy gap values.⁴⁶ On the other hand, the softness is a measure of the polarizability of the chemical.

It should be noted that the soft molecules tend to impart electrons to the metal surface and act as a good corrosion inhibitor. The adsorption of the inhibitor on the metal surface occurs at the molecular moiety with maximum softness and lowest hardness. In the current study, quantum chemical calculations using B3LYP and RHF methods with the 6-311G(d,p) and 6-311++G(2d,2p) basic sets and CBS-Q method were performed to give further insight into the inhibition mechanism of (BTSC, 1), (PCIBTSC, 2), (4DMBTSC, 3) for neutral and protonated forms in gas phase and water phase.

EHOMO and ELUMO are associated with electron donating ability and electron accepting ability of a molecule, respectively. Higher EHOMO is essential for molecular reaction with nucleophiles while lower ELUMO reacts easily with electrophiles.⁴⁷ The order of EHOMO value by using CBS-Q method for the 1, 2, 3 neutral compounds in gas phase is, -8.168 eV, -8.297 eV and -7.539 eV respectively, and for the protonated form of 1, 2, 3 in gas phase is -12.034 eV, -11.963 eV and -10.352 eV, and 1, 2, 3 neutral compounds in water phase, -8.548 eV, -8.604 eV and -7.541 eV and 1, 2, 3 protonated compounds in water phase is -8.954 eV, -8.999 eV - 7.663 eV, respectively (Fig. 3).

Higher the value of EHOMO better will be the inhibition efficiency. The order of EHOMO value of the three investigated species for the neutral and protonated form in gas and water phase is 4DMBTSC (3) > BTSC (1) > PCIBTSC (2) as compatible with the experiment results. The highest value of EHOMO observed 4DMBTSC indicates the better inhibition efficiency. Hence the order of inhibition efficiency based on EHOMO value is 4DMBTSC > BTSC > PCIBTSC. The prediction made from EHOMO values falls in the same line thus proving the validity of the experimental. Experimental inhibition efficiencies have been obtained by Abd-El-Nabey and co-workers in 2012.⁴¹ According to their report, the inhibition efficiency has been given as follows: 4DMBTSC (3) > BTSC (1) > PCIBTSC (2).

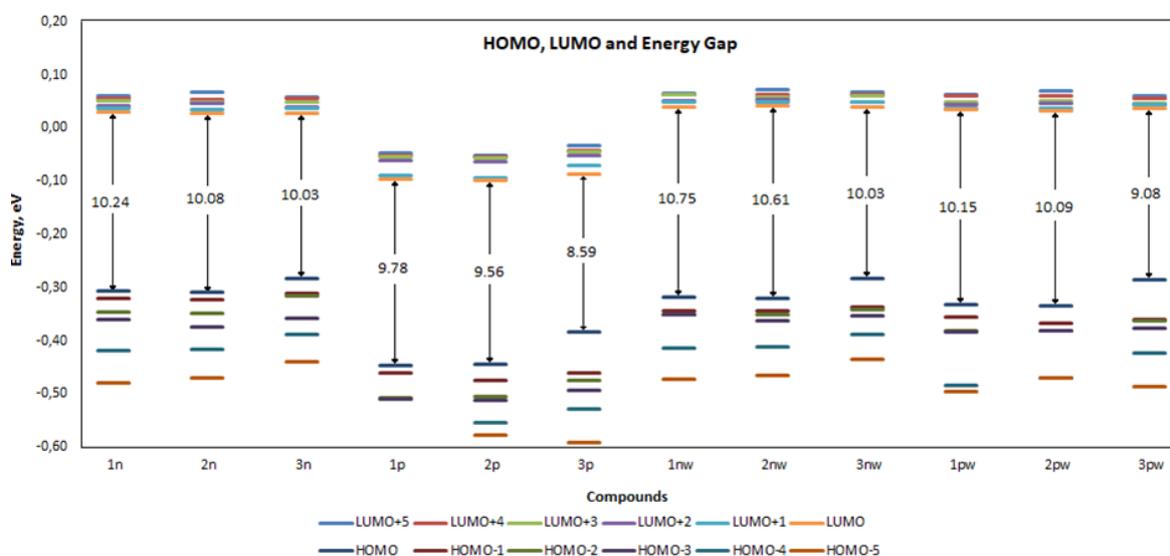


Figure 3. The calculated HOMO, LUMO and energy gap parameters for compounds in the neutral and protonated forms in gas phase and water phase by using CBS-Q basic set

ELUMO shows the ability of the molecule to accept electrons. Lower the value of ELUMO better will be the ability to accept electrons, and so this will improve the adsorption of the inhibitor on the metal surface and therefore better inhibition efficiency. ELUMO values of 1, 2 and 3 molecules are found by using CBS-Q method for neutral phase 2.077, 1.784, 2.492 eV and protonated phase -6.261, -6.341, -5.89 eV, and non-protonated water phase -1.945, -2.074, -1.586 eV, protonated water phase -2.256, -2.401, -1.758 eV, and protonated water phase

1.196, 1.086, 1.414 eV, respectively. According to these results it is clear that, the order of inhibition efficiency for study molecules for the non-protonated and protonated forms in gas and in the presence of water phase can be written as: 4DMBTSC > BTSC > PCIBTSC (Fig. 3). The other calculations made for HOMO and LUMO by using B3LYP and RHF methods with the 6-311G(d,p) and 6-311++G(2d,2p) basic sets can be seen from Figs. 4-7.

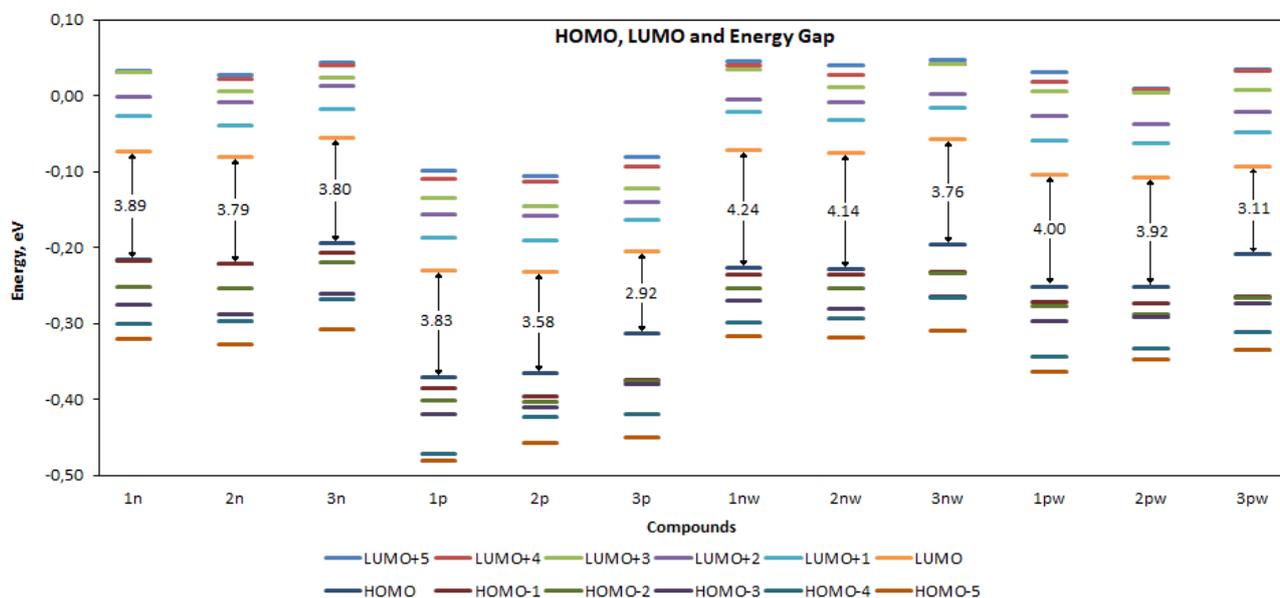


Figure 4. The calculated HOMO, LUMO and energy gap parameters for compounds in the neutral and protonated forms in gas phase and water phase by using B3LYP/6-311G(d,p) basic set

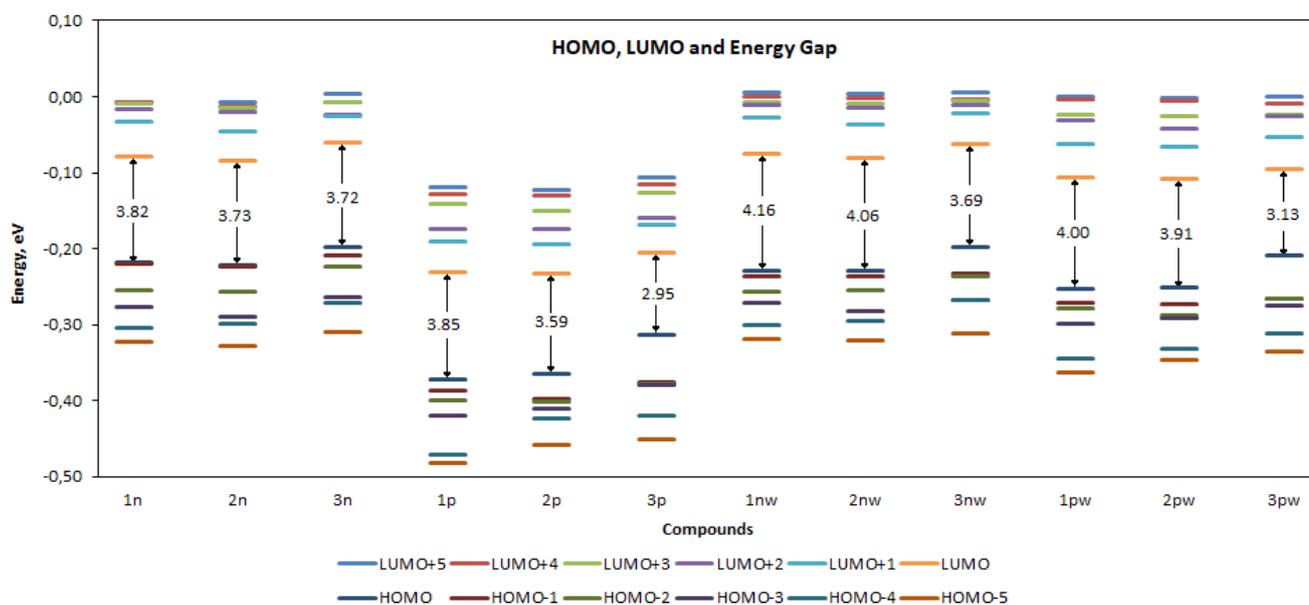


Figure 5. The calculated HOMO, LUMO and energy gap parameters for compounds in the neutral and protonated forms in gas phase and water phase by using B3LYP/6-311++G(2d,2p) basic set

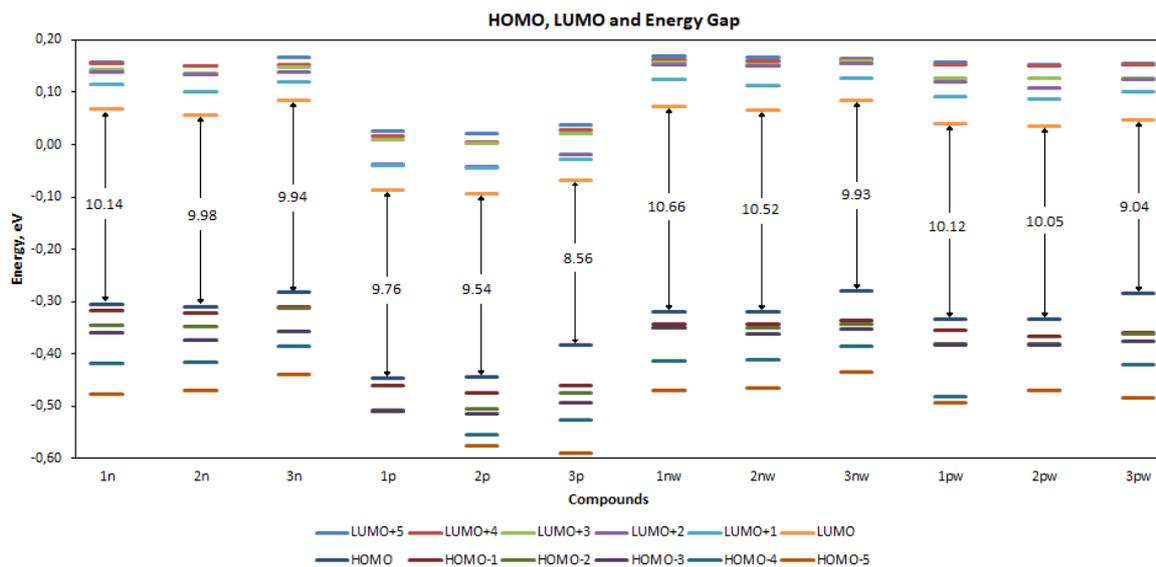


Figure 6. The calculated HOMO, LUMO and energy gap parameters for compounds in the neutral and protonated forms in gas phase and water phase by using RHF/6-311G(d,p) basic set

HOMO-LUMO energy gap (ΔE), chemical hardness and softness are closely related to chemical properties. ΔE value is smaller when the basis set of atomic orbitals are magnified due to the changing of HOMO, usually to a more negative energy and decreasing in energy of LUMO.⁴⁸ If a molecule has a large energy gap, it is called hard and other wise is called soft.[49] More stable molecules have large ΔE value, and lower kinetics stability and higher chemical reactivity have small ΔE value. Concerning the value of the energy gap ΔE , larger values of the energy difference will provide low reactivity to a chemical species.

ΔE values for neutral phase of 1, 2 and 3 molecules were found by using CBS-Q method 10.244, 10.081, 10.031 for gas phase and 10.752, 10.614, 10.026 eV for non-protonated water phase, and 9.777, 9.562, 8.594 eV for protonated phase and 10.150, 10.085, 9.077 eV for protonated water phase, respectively (Fig. 3). Lower values of the ΔE will render good inhibition efficiency, because the energy required to remove an electron from the lowest occupied orbital will be low. ΔE value of 4DMBTSC molecule for protonated in gas phase, neutral and protonated form in water except neutral form in gas phase is the lowest and inhibition efficiency of this substance is the highest one.[41] The other calculations made for ΔE can be seen from Figs. 4-7.

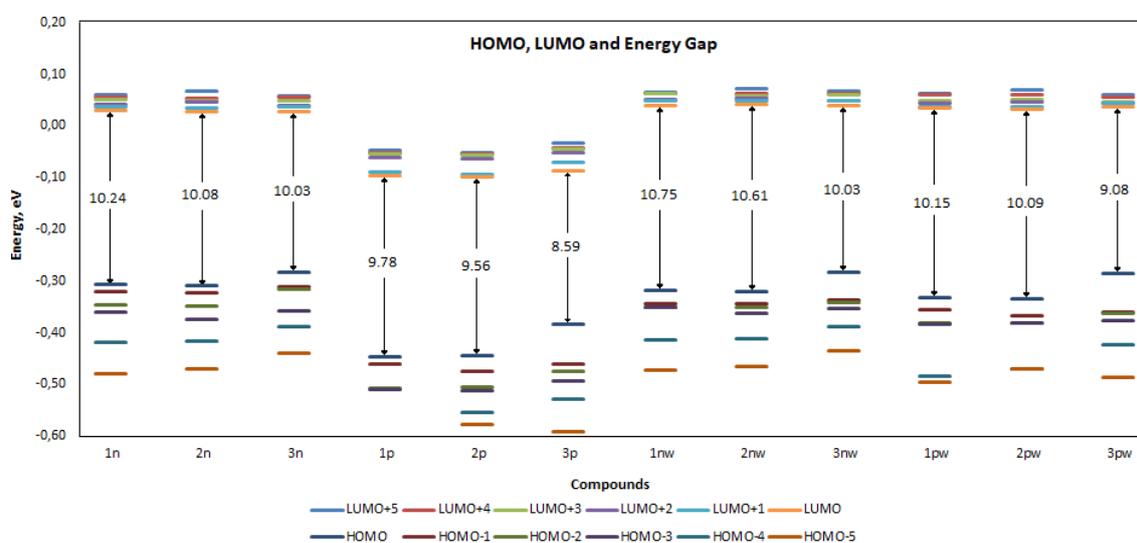


Figure 7. The calculated HOMO, LUMO and energy gap parameters for compounds in the neutral and protonated forms in gas phase and water phase by using RHF/6-311++G(2d,2p) basic set

ΔE values for neutral phase of 1, 2 and 3 molecules were found by using CBS-Q method 10.244, 10.081, 10.031 for gas phase and 10.752, 10.614, 10.026 eV for non-protonated water phase, and 9.777, 9.562, 8.594 eV for protonated phase and 10.150, 10.085, 9.077 eV for protonated water phase, respectively (Fig. 3). Lower values of the ΔE will render good inhibition efficiency, because the energy required to remove an electron from the lowest occupied orbital will be low. ΔE value of 4DMBTSC molecule for protonated in gas phase, neutral and protonated form in water except neutral form in gas phase is the lowest and inhibition efficiency of this substance is the highest one.⁴¹ The other calculations made for ΔE can be seen from Figs. 4-7.

The chemical hardness (η) and softness (σ) are widely used in chemistry for explaining stability of compounds. According to Maximum Hardness Principle,⁴⁸ chemical hardness is a measure of the stability of chemical species. The chemical hardness is just half the energy gap between the EHOMO and ELUMO (see eq. 7). Softness is a measure of the polarizability and soft molecules give more easily electrons to an electron acceptor molecule or surface.⁴⁹ On the basis of the calculated chemical hardness and softness values are given in Table 1. According to softness (σ) values, electron donating trend of studied chemical compounds may be written as: $3 > 2 > 1$ for the neutral and protonated forms in gas and water phase compounds by using all methods (Table 1).

The average values of the HOMO and LUMO energies have been defined as the chemical potential (μ). The chemical potential was defined as the first derivative of the total energy with respect to the number of electrons. The negative of the chemical potential (μ) was known as the electronegativity (χ) (see eq. 6). The chemical potential, electronegativity and hardness are descriptors for the predictions about chemical properties of molecules.⁵⁰ Electronegativity that represents the power to attract the electrons of chemical species is a useful quantity in the prediction of inhibitive performance of molecules.¹ The electronegativity value of 2n is more than those of 1n and 3n for the neutral and protonated forms in gas phase and water phase compounds by using CBS-Q method (see Table 1).

TABLE I. THE CALCULATED QUANTUM CHEMICAL PARAMETERS FOR THE NEUTRAL AND PRONATED FORMS IN GAS PHASE AND WATER PHASE COMPOUNDS BY USING B3LYP AND RHF METHODS WITH THE 6-311G(d,p) AND 6-311++G(2d,2p) BASIC SETS AND CBS-Q METHOD

Compounds	η , eV	σ , eV ¹	χ , eV	μ , eV	ω , eV	ΔE_n , eV	ΔE_o , eV
B3LYP/6-311G(d,p)							
1n	1.947	0.514	3.945	-3.945	3.998	1.026	8.916
2n	1.897	0.527	4.114	-4.114	4.461	1.296	9.524
3n	1.898	0.527	3.403	-3.403	3.052	0.598	7.405
1p	1.916	0.522	8.176	-8.176	17.448	10.229	26.582
2p	1.792	0.558	8.134	-8.134	18.457	11.219	27.486
3p	1.461	0.684	7.048	-7.048	16.995	10.678	24.773
1nw	2.119	0.472	4.064	-4.064	3.896	0.892	9.020
2nw	2.068	0.484	4.141	-4.141	4.148	1.040	9.323
3nw	1.878	0.533	3.464	-3.464	3.194	0.670	7.597

1pw	2.001	0.500	4.860	-4.860	5.903	2.043	11.764
2pw	1.959	0.511	4.893	-4.893	6.110	2.197	11.982
3pw	1.555	0.643	4.120	-4.120	5.457	2.114	10.355
B3LYP/6-311++G(2d,2p)							
1n	1.911	0.523	4.044	-4.044	4.278	1.190	9.277
2n	1.867	0.536	4.186	-4.186	4.694	1.441	9.814
3n	1.860	0.538	3.517	-3.517	3.325	0.738	7.772
1p	1.923	0.520	8.198	-8.198	17.470	10.234	26.630
2p	1.794	0.557	8.131	-8.131	18.424	11.190	27.451
3p	1.473	0.679	7.075	-7.075	16.991	10.653	24.802
1nw	2.077	0.481	4.141	-4.141	4.127	1.025	9.306
2nw	2.030	0.493	4.201	-4.201	4.347	1.161	9.564
3nw	1.843	0.543	3.556	-3.556	3.432	0.797	7.910
1pw	2.000	0.500	4.878	-4.878	5.948	2.070	11.826
2pw	1.953	0.512	4.896	-4.896	6.137	2.218	12.009
3pw	1.564	0.640	4.142	-4.142	5.486	2.126	10.410
RHF/6-311G(d,p)							
1n	5.068	0.197	3.239	-3.239	1.035	0.330	6.807
2n	4.992	0.100	3.438	-3.438	1.184	0.242	7.118
3n	4.969	0.101	2.689	-2.689	0.728	0.523	5.901
1p	4.882	0.102	7.275	-7.275	5.420	0.586	15.136
2p	4.772	0.105	7.301	-7.301	5.585	0.670	15.272
3p	4.279	0.117	6.158	-6.158	4.431	0.413	12.728
1nw	5.328	0.094	3.347	-3.347	1.051	0.368	7.062
2nw	5.262	0.095	3.456	-3.456	1.135	0.310	7.222
3nw	4.964	0.101	2.668	-2.668	0.717	0.531	5.867
1pw	5.060	0.099	4.003	-4.003	1.583	0.110	8.117
2pw	5.026	0.099	4.069	-4.069	1.647	0.091	8.229
3pw	4.520	0.111	3.229	-3.229	1.153	0.184	6.642
RHF/6-311++G(2d,2p)							
1n	4.559	0.219	3.762	-3.762	1.552	0.070	7.594
2n	4.604	0.217	3.823	-3.823	1.587	0.066	7.712
3n	4.230	0.236	3.478	-3.478	1.430	0.067	7.023
1p	4.783	0.209	7.386	-7.386	5.702	0.708	15.479
2p	4.694	0.213	7.361	-7.361	5.771	0.757	15.479
3p	4.048	0.247	6.403	-6.403	5.065	0.685	13.492
1nw	4.887	0.205	3.790	-3.790	1.470	0.123	7.703
2nw	4.918	0.203	3.786	-3.786	1.457	0.130	7.702
3nw	4.382	0.228	3.312	-3.312	1.252	0.131	6.755
1pw	5.013	0.199	4.050	-4.050	1.636	0.093	8.192
2pw	4.979	0.201	4.096	-4.096	1.685	0.078	8.270
3pw	4.363	0.229	3.382	-3.382	1.310	0.110	6.874
CBS-Q							
1n	5.122	0.195	3.046	-3.046	0.905	0.421	6.512
2n	5.040	0.198	3.256	-3.256	1.052	0.316	6.828
3n	5.016	0.199	2.524	-2.524	0.635	0.619	5.666
1p	4.889	0.205	7.145	-7.145	5.221	0.521	14.810
2p	4.781	0.209	7.182	-7.182	5.395	0.603	14.967
3p	4.297	0.233	6.055	-6.055	4.267	0.360	12.470
1nw	5.376	0.186	3.172	-3.172	0.936	0.452	6.796
2nw	5.307	0.188	3.297	-3.297	1.024	0.380	6.975
3nw	5.013	0.199	2.527	-2.527	0.637	0.616	5.671
1pw	5.075	0.197	3.879	-3.879	1.483	0.141	7.899
2pw	5.043	0.198	3.957	-3.957	1.552	0.117	8.030
3pw	4.538	0.220	3.125	-3.125	1.076	0.220	6.469

Electrophilicity (ω) is a useful tool to predict of chemical behaviours of molecules and this quantity can be used to compare the tendency of the inhibitor molecule to accept the electrons.⁵⁰ For this reason, it should be stated that a molecule that has large electrophilicity value is ineffective against corrosion. The trend in which the electrophilicity values (ω) increases is as follows: $2 > 1 > 3$ for the neutral and protonated forms in gas phase and water phase compounds by using B3LYP and RHF methods with the 6-311G(d,p) and 6-311++G(2d,2p) basic sets and CBS-Q method (Table 1). Within framework of this information, we can write the corrosion inhibition efficiency ranking of the molecules as: $3 > 1 > 2$. This ranking is compatible with the experimental inhibition efficiency ranking.

The nucleofugality (ΔE_n) is related to a molecular fragment's ability to accept an electron, a small value for ΔE_n will be associated with a high nucleofugality. Unlike the ΔE_n , ΔE_e measures the energy required to donate an electron to a perfect electron donor.⁴⁵ The nucleofugality values (ΔE_n) were found to be for the neutral form in gas phase as 1.026 eV, 1.296 eV, 0.598 eV by using B3LYP methods with the 6-311G(d,p) basic set and 1.190 eV, 1.441 eV, 0.738 eV with B3LYP/6-311++G(2d,2p) basic set for compounds 1, 2 and 3, respectively. The nucleofugality values (ΔE_n) increases is as follows: $3 < 1 < 2$ for the neutral form in gas phase for this basic sets. According to nucleofugality results, we can write the corrosion inhibition efficiency ranking of the molecules as: $3 > 1 > 2$.

The correlation between the HOMO, LUMO and polarizability values calculated for the neutral and protonated forms in gas phase and water phase of all compounds by using 6-311G(d,p) with 6-311++G(2d,2p) basis sets of the B3LYP and RHF methods is given in Table 2. HOMO was found that the values calculated with 6-311G(d,p) and 6-311++G(2d,2p) basis sets of the B3LYP and RHF methods were close to each other. Similarly, the correlation between the LUMO values calculated and results given in Table 2. It was found that the values calculated with the B3LYP/6-311G(d,p) with 6-311++G(2d,2p) basis sets were close to each other (correlation coefficient, $R^2= 0.999$). The correlation between the HOMO,

LUMO and polarizability values calculated for the neutral and protonated forms in gas phase and water phase compounds by using the RHF/6-311G(d,p) and 6-311++G(2d,2p) basis sets is given in Table 2. The correlation of LUMO values for protonated form in gas phase was found 1.000.

TABLE II. THE CORRELATION BETWEEN B3LYP/311G(D,P) WITH 6-311++G(2D,2P) AND RHF/6-311G(D,P) WITH 6-311++G(2D,2P) BASIS SETS FOR E_{HOMO} , E_{LUMO} AND POLARIZABILITY VALUES

Compounds	HOMO, R^2	LUMO, R^2	Polarizability, R^2
B3LYP/311G(d,p) with 6-311++G(2d,2p)			
Neutral	0.9995	0.9992	0.9992
Pronated	0.9996	0.9995	0.9993
Neutral water	0.9998	0.9990	0.9990
Pronated water	0.9998	0.9995	0.9989
RHF/6-311G(d,p) with 6-311++G(2d,2p)			
Neutral	0.9998	0.5551	0.9983
Pronated	0.9998	1.0000	0.9988
Neutral water	0.9999	0.9401	0.9975
Pronated water	0.9998	0.7045	0.9983

The correlation of inhibition efficiency (IE %) with variable values of the calculated quantum chemical parameters for all compounds in the neutral and protonated forms in gas phase and water phase by using B3LYP and RHF methods with the 6-311G(d,p) and 6-311++G(2d,2p) basic sets and CBS-Q method was found (see Table 3). In general, it appears that the correlation between the notr and protonated molecules is better.

The calculated results with B3LYP/6-311++G(2d,2p) basic set of HOMO, LUMO, energy gap, chemical hardness, softness, electronegativity and chemical potential have been found for protonated phase as 0.9838, 0.9018, 0.9984, 0.9984, 0.9997, 0.9647 and 0.9647 respectively, and 0.9786, 0.8887, 0.9994, 0.9994, 0.9991, 0.9569 and 0.9569 for B3LYP/6-311G(d,p) basic set, respectively. The other results can be seen in Table 3. Generally, between the same rows, there is a good correlation between the reference set and the trend result, and there is no significant difference.

TABLE III. THE CORRELATION COEFFICIENT (R^2) OF INHIBITION EFFICIENCY (IE %) WITH VARIABLE VALUES OF THE CALCULATED QUANTUM CHEMICAL PARAMETERS FOR ALL COMPOUNDS IN THE NEUTRAL AND PRONATED FORMS IN GAS PHASE AND WATER PHASE BY USING B3LYP AND RHF METHODS WITH THE 6-311G(d,p) AND 6-311++G(2d,2p) BASIC SETS AND CBS-Q METHOD

Compounds	EHOMO	ELUMO	ΔE	η	σ	χ	μ	ω	ΔE_n	ΔE_e
B3LYP/6-311G(d,p)										
Neutral	0.8484	0.7290	0.4713	0.4713	0.4808	0.7932	0.7932	0.7075	0.6471	0.7490
Pronated	0.9786	0.8887	0.9994	0.9994	0.9991	0.9569	0.9569	0.3081	0.0351	0.7033
Neutral water	0.9294	0.7692	0.9985	0.9985	0.9969	0.8840	0.8840	0.7703	0.6334	0.8427
Pronated water	0.9456	0.8231	0.9756	0.9756	0.9702	0.9239	0.9239	0.7198	0.0398	0.8717
B3LYP/6-311++G(2d,2p)										
Neutral	0.8639	0.7534	0.6009	0.6009	0.6031	0.8136	0.8136	0.7327	0.6787	0.7711
Pronated	0.9838	0.9018	0.9984	0.9984	0.9997	0.9647	0.9647	0.3335	0.0291	0.7265
Neutral water	0.9358	0.7950	0.9974	0.9974	0.9965	0.8965	0.8965	0.7906	0.6605	0.8572
Pronated water	0.9523	0.8402	0.9797	0.9797	0.9730	0.9323	0.9323	0.7452	0.0106	0.7883
RHF/6-311G(d,p)										
Neutral	0.8542	0.6548	0.6930	0.6930	0.4718	0.7678	0.7678	0.7096	0.7224	0.7778
Pronated	0.9608	0.8165	0.9951	0.9951	0.9973	0.9326	0.9326	0.8657	0.7113	0.9182
Neutral water	0.9249	0.6801	0.9947	0.9947	0.9879	0.8692	0.8692	0.8246	0.7710	0.8823
Pronated water	0.9323	0.7359	0.9658	0.9672	0.9423	0.9050	0.9050	0.8747	0.8182	0.9091
RHF/6-311++G(2d,2p)										
Neutral	0.8630	0.9896	0.8804	0.8804	0.8897	0.8426	0.8426	0.8072	0.3474	0.8461
Pronated	0.9667	0.8192	0.9828	0.9828	0.9787	0.9521	0.9521	0.8940	0.3129	0.9423
Neutral water	0.9309	0.4371	0.9156	0.9156	0.9042	0.9461	0.9461	0.9643	0.5000	0.9430
Pronated water	0.9386	0.1942	0.9621	0.9621	0.9669	0.9126	0.9126	0.8741	0.5844	0.9171
CBS-Q										
Neutral	0.8436	0.6181	0.6981	0.6981	0.7160	0.7482	0.7482	0.6849	0.6895	0.7626
Pronated	0.9583	0.8034	0.9950	0.9950	0.9879	0.9279	0.9279	0.8583	0.6978	0.9133
Neutral water	0.9187	0.6250	0.9961	0.9961	0.9902	0.8525	0.8525	0.8016	0.7351	0.8698
Pronated water	0.9277	0.7013	0.9648	0.9648	0.9589	0.8968	0.8968	0.8635	0.7980	0.9020

IV. CONCLUSIONS

The quantum chemical parameters, EHOMO, ELUMO, Energy gap (ΔE), chemical hardness (η), softness (σ), electronegativity (χ), chemical potential (μ), global electrophilicity (ω), nucleofugality (ΔE_n) and electrofugality (ΔE_e) were found by using B3LYP and RHF methods with the 6-311G(d,p) and 6-311++G(2d,2p) basic sets and CBS-Q method. As a result of these calculations, the order of inhibition efficiency is found 4DMBTSC (3) > BTSC (1) > PCIBTSC (2) as compatible with the experiment results for neutral and pronated forms in gas phase and water phase. The correlation coefficient between the experimental inhibition efficiency (IE %) and theoretical results was found using the theoretical results. There was no significant difference between the reference set and the trend results ($R^2 = 0.9988$ and $R^2 = 0.9993$), between the same rows.

REFERENCES

- [1] S. Kaya, C. Kaya, L. Guo, F. Kandemirli, B. Tüzün, İ. Uğurlu, L.H. Madkour, M. Saracoglu, J. Mol. Liq. 219 (2016) 497-504.
- [2] S.N. Raicheva, B.V Aleksiev, E.I. Sokolova, Corros. Sci. 34 (1993) 343-350.
- [3] S. Kaya, B. Tüzün, C. Kaya, I.B. Obot, J. Taiwan Inst. Chem. Eng. 58 (2016) 528-535.
- [4] M. Elayyachy, B. Hammouti, A. El Idrissi, Appl. Surf. Sci. 249 (2005) 176-182.
- [5] M. Bouklah, B. Hammouti, M. Lagrenee, F. Bentiss, Corros. Sci. 48 (2006) 2831-2842.
- [6] M. Ajmal, A. S. Mideen, M.A. Quraishi, Corros. Sci. 36 (1994) 79-84.
- [7] N. Caner, I.A.N. Love, Int. J. Quantum Chem. 110 (2010) 1003-1018.
- [8] M.A. Amin, M.A. Ahmed, H.A. Arida, T. Arslan, M. Saracoglu, F. Kandemirli, Corros. Sci. 53 (2011) 540-548.
- [9] S. Zor, M. Saracoglu, F. Kandemirli, T. Arslan, Corrosion. 67 (2011) 125003-1-125003-11 (11 pages).
- [10] M.A. Amin, O.A. Hazzazi, F. Kandemirli, M. Saracoglu, Corrosion. 68 (2012) 688-698.
- [11] F. Kandemirli, M. Saracoglu, M.A. Amin, M.A. Basaran, C.D. Vurdu, Int. J. Electrochem. Sci. 9 (2014) 3819-3827.
- [12] M.A. Amin, N. El-Bagoury, M. Saracoglu, M. Ramadan, Int. J. Electrochem. Sci. 9 (2014) 5352-5374.
- [13] F. Kandemirli, C.D. Vurdu, M. Saracoglu, Y. Akkaya, M.S. Cavus, Int. Res. J. Pure and Applied Chem. 9 (2015) 1-16.
- [14] N. El-Bagoury, M.A. Amin, M. Saracoglu, Int. J. Electrochem. Sci. 10 (2015) 5291-5308.
- [15] M.A. Amin, S.A. Fadlallah, G.S. Alosaimi, F. Kandemirli, M. Saracoglu, S. Szunerits, R. Boukherroub, Int. J. Hyd. Energy. 41 (2016) 6326-6341.

- [16] A. Tazouti, M. Galai, R. Touir, M. Ebn Touhami, A. Zarrouk, Y. Ramli, M. Saraçoğlu, S. Kaya, F. Kandemirli, C. Kaya, *J. Mol. Liq.* 221 (2016) 815-832.
- [17] M.A. Amin, M. Saracoglu, N. El-Bagoury, T. Sharshar, M.M. Ibrahim, J. Wysocka, S. Krakowiak, J. Ryl, *Int. J. Electrochem. Sci.* 11 (2016) 10029-10052.
- [18] E.E. Ebenso, T. Arslan, F. Kandemirli, I. Love, C. Öğretir, M. Saracoglu, S.A. Umoren, *Int. J. Quantum Chem.* 110 (2010) 2614-2636.
- [19] F. Bentiss, M. Lebrini, M. Lagrenée, *Corros. Sci.* 47 (2005) 2915-2931.
- [20] D. Wang, S. Li, Y. Ying, M. Wang, H. Xiao, Z. Chen, *Corros. Sci.* 41 (1999) 1911-1919.
- [21] E.S. H. El Ashry, A. El Nemr, S.A. Esawy, S. Ragab, *Electrochim. Acta.* 51 (2006) 3957-3968.
- [22] J. Fang, J. Li, *J. Mol. Struct. THEOCHEM.* 593 (2002) 179-185.
- [23] F. Kandemirli, S. Sağdıç, *Corros. Sci.* 49 (2007) 2118-2130.
- [24] A. Yurt, G. Bereket, C. Oğretir, *J. Mol. Struct. THEOCHEM.* 725 (2005) 215-221.
- [25] H. Ma, S. Chen, Z. Liu, Y. Sun, *J. Mol. Struct. THEOCHEM.* 774 (2006) 19-22.
- [26] T. Arslan, F. Kandemirli, E.E. Ebenso, I. Love, H. Alemu, *Corros. Sci.* 51 (2009) 35-47.
- [27] A. Nakayama, K. Hagiwara, S. Hashimoto, S. Shimoda, *Mol. Inform.* 1993, 12, 251-255.
- [28] M.A. Amin, M.A. Ahmed, H.A. Arida, F. Kandemirli, M. Saracoglu, T. Arslan, M.A. Basaran, *Corros. Sci.* 53 (2011) 1895-1909.
- [29] M. Lebrini, F. Robert, H. Vezin, C. Roos, *Corros. Sci.* 52 (2010) 3367-3376.
- [30] I.B. Obot, N.O. Obi-Egbedi, *Corros. Sci.* 52 (2010) 657-660.
- [31] D.K. Yadav, B. Maiti, M.A. Quraishi, *Corros. Sci.* 52 (2010) 3586-3598.
- [32] D. Özkır, K. Kayakırılmaz, E. Bayol, A.A. Gürten, F. Kandemirli, *Corros. Sci.* 56 (2012) 143-152.
- [33] E.E. Ebenso, M.M. Kabanda, T. Arslan, M. Saracoglu, F. Kandemirli, *Corros. Sci.* 7 (2012) 5643-5676.
- [34] S.S. Mahmoud, *J. Mater. Sci.* 42 (2007) 989-997.
- [35] M. Maji, M.M. Nandi, *Ind. J. Chem. Tec.* 16 (2009) 221-227.
- [36] R. Zhang, P. Somasundaran, *Adv. Colloid Interface Sci.* 123 (2006) 213-229.
- [37] Y. Sürme, A.A. Gürten, E. Bayol, *Prot. Met. Phys. Chem. Sur.* 47 (2011) 117-120.
- [38] D. Özkır, E. Bayol, A.A. Gürten, Y. Sürme, F. Kandemirli, *Chem. Papers.* 67 (2013) 202-212.
- [39] E.E. Ebenso, U.J. Ekpe, B.I. Ita, O.E. Offiong, U.J. Ibok, *Mater. Chem. Phys.* 60 (1999) 79-90.
- [40] G.E. Badr, *Corros. Sci.* 51 (2009) 2529-2536.
- [41] B.A. Abd-El-Nabey, A.M. Abdel-Gaber, G.Y. Elewady, M.M. El Sadeek, H. Abd-El-Rhman, *Int. J. Electrochem. Sci.* 7 (2012) 11718-11733.
- [42] N. Karakus, K. Sayin, *J. Taiwan Inst. Chem. Eng.* 2015, 48, 95-102.
- [43] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc. Wallingford CT, 2016.
- [44] R.G. Parr, R.G. Pearson, *J. Am. Chem. Soc.* 105 (1983) 7512-7516.
- [45] L. Gao, H. Wang, X. Song, W. Cao, *J. Mol. Struct.* 1034 (2013) 386-391.
- [46] R.G. Pearson, *J. Am. Chem. Soc.* 85 (1963) 3533-3539.
- [47] A. Rank, *Orbital Interaction Theory of Organic Chemistry*, 2nd ed; Wiley & Sons: New York, 2001.
- [48] R.G. Pearson, *Acc. Chem. Res.* 26 (1993) 250-255.
- [49] R.G. Pearson, *Proceedings of the National Academy of Sciences of the USA.* 83 (1986) 8440-8441.
- [50] A. Özalp, Z. Kökbudak, M. Saracoglu, F. Kandemirli, İ.Ö. İlhan, C.D. Vurdu, *Chem. Sci. Rev. Lett.* 4 (2015) 719-728.