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Theoretical study of some methyl and fluoride derivatives of bis-piperidiniummethyl-thiourea as corrosion inhibitors

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ABSTRACT

Density functional theory is situated within the evolution of quantum chemistry as a facilitator of computations and a provider of new chemical insights. Various electronic reactivity indices related to ρ (r), such as Fukui function (FF), condensed Fukui function (CFF) and dual descriptor (DD) have been identified. Some methyl and fluoride derivatives of Bis-piperidiniummethyl-thiourea (BPMTU) as like as urea derivatives compounds can be designed as corrosion inhibitors and they were studied in the present work. We obtained a correlation relationship related to these novel compounds to predict inhibition of efficiency against the corrosion of mild steel in hydrochloric acid solution. The reactive sites with negative and positive dual descriptor were determined for each molecule. The calculations showed that several parameters as a nonlinear relationship are taken into account to characterize the inhibition activity of the designated compounds.

KEYWORDS

Corrosion Inhibitor;
Bis-piperidiniummethyl-thiourea;
Dual descriptor;
Density functional theory (DFT);
Correlation relationship.

INTRODUCTION

Nitrogen-heterocyclic compounds are usually used as inhibitors for metals in acidic medium and many experiments have been done in this aspect[1-5]. Experiments are useful in explaining the inhibition mechanism but they are often expensive and time consuming. Quantum chemistry methods are powerful tool for investigation structural parameters and also provide a wider vision than the level of interaction between inhibitor and surface. During the development of the quantum chemical methods, Klopman[6] and Pearson[7] derived a method for the calculation of the properties of chemical systems and the bonding that is involved in the molecular systems. Quantum chemical methods are usually used to explore the relationship between the inhibitor molecular properties and its corrosion inhibition efficiency[8].

Zhang and coworkers[9] studied bis-piperidiniummethyl-urea (BPMU) and mono-piperidiniummethyl-urea (MPMU) (scheme I) as novel volatile corrosion inhibitors. They investigated quantum chemical parameters using PM3 semi-empirical method. The results showed that BPMU had better protective effect for mild steel and had lower E_{HOMO} and E_{LUMO} values compared with MPMU. BPMU was better inhibitor and had the smaller HOMO–LUMO gap compared with MPMU.

Fang and Li[10] performed quantum chemical calculations on urea (U), thiourea (TU), thioacetamide (TA) and thiosemicarbazide (TSC), using the MINDO/3 method. They found a correlation between corrosion inhibition efficiency and some quantum chemical parameters. Ebenso and coworkers[11] studied corrosion inhibition efficiency of these compounds. A detailed quantum chemical calculations have been performed for some amides and thiosemicarbazones using semi-empirical, density functional theory (DFT), ab initio molecular orbital methods by Kandemirli and Sagdinc[12].

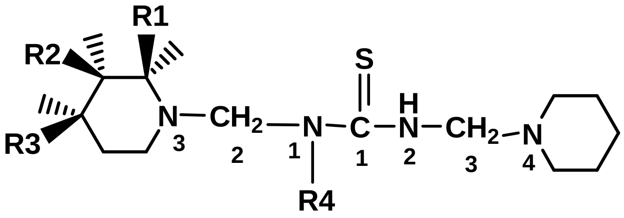
Predicting and understanding the chemical reactivity and selectivity for particular atomic centers in a reactant molecule have been of importance in physical-organic chemistry, especially for the molecules possessing two or more nucleophilic or electrophilic reactive centers. Fukui functions (FF) have been found to be useful intermolecular reactivity descriptors for nucleophilic and electrophilic reactions[13].

In order to investigate the improvement of the chemical reactivity and selectivity of BMPU, in this paper we selected the bis-piperidiniummethyl-thiourea (PMPTU), molecule No 1 in figure 1, as the base and some methyl and fluoride substituted of the hypothetic compound were designed. They are derivated by substituted methyl and fluoride groups on the N (3) atom (R4) and/or as substituted groups of R1, R2, or R3 in peridinium ring of BPMTU, as depicted in figure 1. The aim of this paper is to introduce these novel compounds with possible corrosion inhibition properties. For this purpose, we investigated the full optimized geometry of each hypothetic compound in both gas and acidic solution phases by DFT method and evaluated the electronic properties related to behavior of corrosion inhibition. Another objective is the finding a correlation relationship to predict inhibition efficiency for the compounds by fitting the best relationship between the molecular electronic properties and experimental data of inhibition efficiencies of some compounds whose molecular geometries near to these hypothetical compounds. Moreover we are trying to determine the nucleophilic and electrophilic centers in the considered compounds.

BPMU

MPMU

Scheme 1



No	R_1	R_2	R_3	R_4
1	H	H	H	H
2	CH_3	H	H	H
3	H	CH_3	H	H
4	H	H	CH_3	H
5	H	H	H	CH_3
6	F	H	H	H
7	H	F	H	H
8	H	H	F	H
9	H	H	H	F

Figure 1 : Bis-piperidiniummethyl-thiourea and derivatives

THEORY AND COMPUTATIONAL DETAILS

Fukuifunctions (FF)

The formal definition of Fukui function (FF) within density functional theory (DFT) is given by:

$$f(\vec{r}) = (\frac{\partial \rho}{\partial N})_{V(\vec{r})} = [\frac{\delta \mu}{\delta V(\vec{r})}]_N \qquad (1)$$

Owning to discontinuity of the ñ (r) vs. curve, we have three possible derivatives as follow[14,15]:

$$f^{\alpha}(r) = (\frac{\partial \rho(r)}{\partial N})^{\alpha}_{V(r)} \quad \alpha = + \text{ or } - \text{ or } 0 \qquad (2)$$

where the superscript, α, allows us to have three different types of Fukui function: f^-_k for electrophilic attack, f^+_k for nucleophilic attack and f^0_k, which measures the radical reactivity. Yang and Parr have proposed a finite difference scheme to evaluate f (r)[16],

$$f^{+}(r) \cong \rho_{N+1}(r) - \rho_{N}(r) \qquad (3)$$

$$f^{-}(r) \cong \rho_{N}(r) - \rho_{N-1}(r) \qquad (4)$$

where $\rho_{N+1}(r)$, $\rho_{N}(r)$ and $\rho_{N-1}(r)$ are the electronic densities of the system with N+1, N and N-1 electron, respectively. Similarly, the finite difference approximation leads to the condensed Fukui function f_k[17,18],

$$f_k^{+}(r) = q_k(N+1) - q_k(N) \qquad (5)$$

$$f_k^{-}(r) = q_k(N) - q_k(N-1) \qquad (6)$$

The gross charge q_k of atom k is generally calculated from a Mulliken population analysis and the terms q_k (N+1) and q_k (N-1) are calculated at the same geometry of the N electron system.

It has been previously believed that the Taylor expansion up to the second order in the following equation should be adequate for descriptions of most chemical processes[19]:

$$\Delta E = \left(\frac{\partial E}{\partial N}\right)_V \Delta N + \int \left(\frac{\partial E}{\partial V(r)}\right)_N \delta V(r) d(r) + \frac{1}{2!}\{\left(\frac{\partial^2 E}{\partial N^2}\right)_V \Delta N^2 + \ldots \qquad (7)$$

Nevertheless, recent progresses demonstrate that amazing results can be obtained when third-order derivatives from cross terms are considered[20]. These new reactivity indices are called dual descriptors because the same quantity can be at one and the same time an indicator for both the nucleophilic and electrophilic regions of a molecule. In 2005, Morell, Grand and Toro-Labbe[21] proposed the first dual descriptor using the third order derivatives:

$$f^2(r) = \left(\frac{\partial^2}{\partial^2 N}\left(\frac{\delta E}{\delta V(r)}\right)_N\right)_V = \left(\frac{\delta}{\delta V(r)}\left(\frac{\partial^2 E}{\partial^2 N}\right)_V\right)_N = \left(\frac{\partial f(r)}{\partial N}\right)_V = \left(\frac{\delta \eta}{\delta V(r)}\right)_N \qquad (8)$$

Since the Fukui function is normalized, the normalization condition for $f^2(r)$ is as follows:

$$\int f^2(r) dr = 0 \qquad (9)$$

Under the finite difference approximation[22] and using Eqs. (3) and (4) we have:

$$f^2(r) = \Delta f = f^{+}(r) - f^{-}(r) \qquad (10)$$

These results show that $f^2(r)$ will be positive in electrophilic regions, and negative in nucleophilic regions.

Computational method

All calculations and geometry optimization for each molecule and the corresponding cation and anion were obtained by the DFT at the level of the B3LYP/6-31G**[23]. Computational calculations have been performed both in the gaseous phase and in the acid solution in Gaussian 98[24]. The restricted method is used for the neutral systems, whereas the unrestricted method is used for the corresponding anion and cation calculations. The geometry of all molecules under investigation was determined by optimizing all geometrical variables without any symmetry constraints. The harmonic frequencies were computed from analytical derivatives for all species in order to define the minimum-energy structures.

The effect of solute-solvent interaction was taken into account via the self-consistent reaction field (SCRF) method. This method is based on Onsager's reaction field theory of electrostatic solvation and the solvent as a continuous of uniform dielectric constant (ε) and the solute is placed in a cavity within it[25]. For the acidic solution we apply the regression method[26,27] to evaluate the dielectric constant for a binary solution of HCl and H_2O as two constituents of hydrochloric acid solution. The concentration of the acid was 0.25 M and hence the calculated dielectric constant was near about water (ε_{mix}=70.67, and ε_{water}=78.39). Then we used the water as solvent in the SCRF calculations.

The local reactivity has been analyzed by means of Fukui indices which are a representation of the reactive centers within the molecules. These are measurements of the chemical reactivity, as well as a representative of the reactive regions, nucleophilic and electrophilic behavior of the molecule. The condensed Fukui functions are found by taking the finite difference approximations from Mulliken population analysis[17] of atoms in BPMTU derivatives, depending on the direction of the electron transfer.

RESULTS AND DISCUSSION

Global hardness

The results of full geometry optimization including the frontier orbital's, E_{HOMO} and E_{LUMO}, gap energy, ΔE, dipolemoment, μ, and hardness, η, for each molecule are considered for both gas phase and acidic medium and they are collected in TABLE 1. In TABLE 1 these properties were calculated for the molecules 1-9 in gaseous and watery phase with B3LYP/6-31G** chemistry model. The global hardness, η, is approximated as $\Delta E/2$, which is parameter that gives important information about the reactive behavior of the molecule. There are no significant changes in the global hardness of the derivatives in aqueous solution respect to the gas phase. The amounts of the global hardness indicate that the reactivity order for the derivatives in both gas and aqueous phases is:

8>7>6>1>2>4>3>5>9

The compound 8 exhibits the maximum hardness value, whereas the compound 9 presents the minimum value of hardness. The substitution of the fluorine as electroacceptor group on carbon atom in peridiniuom ring of BPMTU increases the hardness of BPMTU, whereas on N (1) atom of the chain of BPMTU deceases the hardness. In contrast, the methyl substitution as an electrodonor group on these positions decreases the hardness of BPMTU. The methyl substitution with low distance from the thiocarbamoyl group leads to less decreasing hardness, and the fluorine substitution causes to more increasing hardness. There is one exception in this observation for the fluorine substitution on N (1) atom. This is probably due to the resonance effect of fluorine with the thiocarbamoyle functional group. This trend is been observing in both phases.

Fukui indices

It has been proven that local electron densities or charges are important in many chemical reactions and physicochemical properties of compound[28]. In order to know the reactivity of compounds and their possible application as corrosion inhibitors, charge on atoms, FF indices, and dual descriptors for all the charged species (N+1 and N-1) as well as the neutral (N) of nine entitled molecules were calculated in gas phase and the results have been collected in TABLES 2 and 3. A Mulliken population analysis were performed for every compound and the results showed that nitrogen and sulfur atoms carry negative charges and have a large electronic density which could make them nucleophilic centers when interacting with the metallic surfaces. This indicated that these atoms are the negative charge centers which could offer electrons to the metal surface to form a coordinate type of bond. But there are exceptional cases about molecule No 2 in which all chain carbons have the negative charges, so they can be considered as nucleophilic centers. As a result, we can not clearly indicate these centers only by charge analysis. Thus we notified to the double descriptors.

The analysis of the values of DD showed that the nucleophilic centers in molecule 1 are N (1), N (2), N (3), N (4), C (2), and S. For molecule 2 they are N (1), N (2), N (3), N (4), C (1), C (2), C (3) and S. For molecule 3 they are N (1), N (2), C (1) and S atoms. For molecule 4 they are N (1), N (2), N (3), C (1), C (2) and S atoms. For molecule 5 they are N (1), C (1), C (2), C (3) and S atoms. For molecule 6 they are C (3) and S atoms. For molecule 7 they are C (3) and S atoms. For molecule 8 they are C (1), C (3) and S atoms. These centers are N (1), N (3), C (1) and C (3) atoms for molecule 9. In all molecules unless 9, the S atom plays role as an nucleophilic center for accepting electrons from metallic atom in corrosion inhibition and the substitution groups decrease the ability of this center as electroacceptor. The highest negative and positive values of DD for S atom are in the molecules 5 and 9, respectively, with respect to BPMTU. It means that the methyl and fluorine substitutions on R4 can promote and demotion the nucleophilic center of S atom, respectively.

The electrophilic regions in these molecules are C (1) and C (3) in molecule 1, N (3), N (4), C (2) and C (3) in molecule 3, N (4) and C (3) in molecule 4, N (2), N (3), N (4) and C (methyl) in molecule 5, N (1), N (2), N (3), N (4), C (1) and C (2) in molecule 6, N (1), N (2), N (3), N (4) C (1) and C (2) in molecule 7, N (1), N (2), N (3), N (4) and C (2) in molecule 8, and N (2), N (4), C (2) and S in molecule 9. There are not any such regions in molecule 2. By this analyzing the site of S atom is very important position role in the electron-interaction of the molecules with the metallic surface during corrosion inhibition process. For confirming such theoretical evaluation, we need to obtain the correlated relationship between the above mentioned quantum parameters and theoretical inhibition efficiencies for these molecules as the following subsection.

TABLE 1 : Quantum chemical parameters for the studied compounds calculated in the gaseous and liquid phase by B3LYP/6- 31G (in a.u.)**

		Gas phase			
NO	E_{HOMO}	E_{LUMO}	EΔ	(Debye)μ	η
1	-0.19254	-0.00334	0.18910	5.35800	0.09460
2	-0.19014	-0.00178	0.18836	5.29410	0.09418
3	-0.19013	-0.00179	0.18834	6.20410	0.09417
4	-0.19015	-0.00191	0.18824	5.23170	0.09412
5	-0.18984	-0.00515	0.18469	5.20100	0.09234
6	-0.18927	0.01527	0.20454	4.61980	0.10227
7	-0.19690	0.00913	0.20603	3.65640	0.10301
8	-0.19495	0.01203	0.20698	4.38830	0.10349
9	-0.20313	-0.02337	0.17976	2.7886	0.08988
			Liquid phase		
1	-0.19868	-0.00619	0.19249	6.79650	0.09624
2	-0.19786	-0.00549	0.19237	7.06700	0.09618
3	-0.19796	-0.00569	0.19227	8.95600	0.09613
4	-0.19707	-0.00512	0.19195	7.01010	0.09597
5	-0.19554	-0.00806	0.18748	6.69000	0.09374
6	-0.19284	0.00049	0.19333	6.03211	0.09666
7	-0.20205	0.00180	0.20385	3.65593	0.10195
8	-0.19543	-0.0088	0.20423	5.91590	0.10211
9	-0.20511	-0.02356	0.18155	3.49330	0.09077

Corrosion inhibition efficiencies

The main objective of this research is finding a relationship between quantum chemical parameters and corrosion inhibition efficiency for molecules 1-9. Since the studied compounds are designed in the base of bis-piperidiniummethyl-thiourea and they have not been synthesized so far, we should operate through indirect for predict corrosion inhibition efficiency. We try to find an equation to fit the experimental and theory data for the molecules close to the structure of the designed molecules, and then this relationship was developed to the title compounds.

The analogous calculations in above sections of this paper were carried out for seven derivatives of thiourea molecules: thioacetamide (TA), thiourea (TU), N-methylthiourea (MTU), thiosemicarbazide (TSC), thiocarbohydrazide (TCH), N-ethylthiourea (ETU), and tetramethylthiourea (TMTU), which the experimental corrosion inhibition efficiencies have been reported[9,29] in hydrochloric acid solution. They were optimized molecular structures by the DFT at the level of the B3LYP/

TABLE 2 : Calculated Mulliken atomic charge and Fukui function (f^+k, f^-k) and dual descriptor (f^2) for the compounds 1-5 in the gas phase using B3LYP/6- 31G (in a.u.)**

	Atom	q_N	q_{N+1}	q_{N-1}	f^+k	f^-k	f^2
1	S	-0.3408	-0.3986	-0.3295	-0.0577	-0.0112	-0.0464
	N(1)	-0.4795	-0.4996	-0.4674	-0.0201	-0.0121	-0.0080
	N(2)	-0.4738	-0.4989	-0.4574	-0.0251	-0.0164	-0.0086
	N(3)	-0.4066	-0.4284	-0.3880	-0.0218	-0.0188	-0.0032
	N(4)	-0.4050	-0.4280	-0.3834	-0.0229	-0.0215	-0.0014
	C(1)	0.2800	0.3132	0.2767	0.0332	0.0032	0.0300
	C(2)	0.0450	0.0473	0.0402	0.0023	0.0048	-0.0024
	C(3)	0.0450	0.0471	0.0435	0.0021	0.0014	0.0006
2	S	-0.3607	-0.4200	-0. 3069	-0.0592	-0.0538	-0.0054
	N(1)	-0. 4983	-0.5181	-0.4798	-0.0197	-0.0184	-0.0013
	N(2)	-0.4801	-0.4932	-0.4725	-0.0130	-0.0076	-0.0054
	N(3)	-0.4266	-0.4526	-0.4087	-0.0259	-0.0179	-0.0080
	N(4)	-0.4052	-0.4257	-0.3883	-0.0205	-0.0169	-0.0035
	C(1)	-0.2409	-0.2780	-0.2200	-0.0370	-0.0209	-0.0160
	C(2)	-0.4802	-0.5069	-0.4579	-0.0267	-0.0222	-0.0044
	C(3)	-0.0430	-0.0465	-0.0415	-0.0035	-0.0014	-0.0020
3	S	-0.3566	-0.4172	-0.3006	-0. 0605	-0.0560	-0.0044
	N(1)	-0.4827	-0.5078	-0.4812	-0.0251	-0.0014	-0.0236
	N(2)	-0.4797	-0.4850	-0.4868	-0.0053	0.0070	-0.0124
	N(3)	-0.4021	-0.4226	-0.3899	-0.0205	-0.0122	-0.0082
	N(4)	-0.4036	-0.4200	-0.3807	-0.0163	-0.0229	0.0065
	C(1)	0.2916	0.1123	0.2708	-0.1792	0.0208	-0.0200
	C(2)	-0.4858	-0.4949	-0.4789	-0.0090	-0.0069	-0.0021
	C(3)	0.0460	0.0508	0.0430	0.0048	0.0297	0.0018
4	S	-0.3434	-0.3776	-0.3100	-0.0342	-0.0334	-0.0008
	N(1)	-0.4754	-0.4938	-0.4688	-0.0183	-0.0066	-0.0117
	N(2)	-0.4802	-0.4989	-0.4853	-0.0187	0.0051	-0.0238
	N(3)	-0.3945	-0.4096	-0.3115	-0.0151	-0.0829	0.0678
	N(4)	-0.4052	-0.3781	-0.4088	0.0271	0.0036	0.0234
	C(1)	0.2892	0.1114	0.2668	-0.1778	0.0224	-0.2002
	C(2)	0.0445	0.0674	0.0342	0.0228	0.0103	0.0124
	C(3)	0.0450	0.0499	0.0407	0.0049	0.0042	0.0006
5	S	-0.3604	-0.4397	-0.3497	-0.0792	-0.0107	-0.0685
	N(1)	-0.4867	-0.5065	-0.4759	-0.0197	-0.0108	-0.0089
	N(2)	-0.5036	-0.4965	-0.4935	0.0070	-0.1005	0.0171
	N(3)	-0.5036	-0.4965	-0.4935	0.0070	-0.1005	0.0171
	N(4)	-0.4114	-0.3818	-0.4175	0.0296	0.0060	0.0236
	C(1)	0.2967	0.1038	0.2717	-0.1929	0.0250	-0.2180
	C(2)	-0.4854	-0.4938	-0.4798	-0.0083	-0.0056	-0.0027
	C(3)	0.0463	0.0518	0.0380	0.0055	0.0082	-0.0026
	C (methyl)	-0.1789	-0.1800	-0.1690	-0.0010	-0.0099	0.0089

6-31G** and the results of obtained parameters as E_{HOMO}, E_{LUMO}, gap energy, and dipole moment have been listed in TABLE 4 and it was showed that dominant molecular parameter for the inhibition effect is the ionization potential, $I=-E_{HOMO}$, and there is a clear relation between the increase in corrosion inhibition and the decrease of the ionization potential.

TABLE 3 : Calculated Mulliken atomic charge and Fukui function (f^+k, f^-k) and dual descriptor (f^2) for the compounds 6-9 in the gas phase using B3LYP/6- 31G (in a.u.)**

	Atom	q_N	q_{N+1}	q_{N-1}	f^+k	f^-k	f^2
6	S	-0.3090	-0.3398	-0.2785	-0.0308	-0.0304	-0.0003
	N (1)	-0.5158	-0.4768	-0.5232	0.0390	0.0073	0.0316
	N (2)	-0.5191	-0.4917	-0.5135	0.0274	-0.0056	0.0330
	N (3)	-0.4180	-0.4314	-0.4022	-0.0134	-0.0156	0.0022
	N (4)	-0.4241	-0.4021	-0.4085	0.0220	-0.0156	0.0376
	C (1)	0.3600	0.4079	0.3449	0.0479	0.0150	0.0328
	C (2)	0.0678	0.1414	0.5085	0.0735	0.0170	0.0565
	C (3)	0.0457	0.0491	0.0304	0.0033	0.0152	-0.0119
7	S	-0.3186	-0.3398	-0.2986	-0.0212	-0.0199	-0.0012
	N (1)	-0.4801	-0.4982	-0.4571	-0.0181	-0.0229	0.0048
	N (2)	-0.4857	-0.4972	-0.4493	-0.0115	-0.0363	0.0248
	N (3)	-0.4117	-0.3842	-0.4331	0.2744	0.0213	0.0048
	N (4)	-0.4041	-0.4278	-0.3082	-0.0237	-0.0958	0.0720
	C (1)	0.3428	0.0369	0.3214	0.0026	0.0021	0.0005
	C (2)	0. 2979	0.3322	0.2765	0.0342	0.0213	0.0129
	C (3)	0.0459	0.0491	0.0301	0.0033	0.0158	-0.0126
8	S	-0.3185	-0.3590	-0.2900	-0.0404	-0.0285	-0.0119
	N (1)	-0.5134	-0.5000	-0.5177	0.0134	0.0042	0.0091
	N (2)	-0.5202	-0.4980	-0.5110	0.0222	-0.0091	0.0313
	N (3)	-0.4295	-0.3831	-0.3719	0.4636	-0.0576	0.1039
	N (4)	-0.4381	-0.4281	-0.4130	0.0100	-0.0250	0.0350
	C (1)	0.3533	0.1136	0.3669	-0.2400	-0.1337	-0.2266
	C (2)	-0.4855	-0.5038	-0.4588	-0.0182	-0.0267	0.0084
	C (3)	0.0479	0.0491	0.0295	0.0011	0.0184	-0.0173
9	S	-0.2983	-0.4568	0.0437	-0.1585	-0.3420	0.1840
	N (1)	-0.1042	-0.3540	-0.1039	-0.2498	-0.0003	-0.2500
	N (2)	-0.4991	-0.4878	-0.4838	0.0113	-0.0153	0.0270
	N (3)	-0.3909	-0.4281	-0.3578	-0.0372	-0.0331	-0.0040
	N (4)	-0.4270	-0.4202	-0.3986	0.0068	-0.0284	0.0350
	C (1)	0.3303	0.3229	0.3166	-0.0074	0.0137	-0.0210
	C (2)	0.0764	0.1429	0.0781	0.0665	-0.0017	0.0550
	C (3)	0.0965	0.0684	0.0696	-0.0281	0.0269	-0.0550

TABLE 4 : E_{HOMO}, E_{LUMO}, gap energy (ΔE) and dipole moments (μ) (in a. u.) for seven derivatives of thiourea compounds with experimental inhibition efficiencies (IE %) calculated in the aqueous phase by B3LYP/6- 31G method and the calculated IE% for the titled compounds (1-9) accordance to the eq. (12)**

Name	E_{HOMO}	E_{LUMO}	ΔE	μ	IE%[a]	No	IE% (cal)
TA	-0.2120	-0.0311	0.1816	6.4373	56	1	75
TU	-0.2066	0.0091	0.2157	7.0400	72	2	77
MTU	-0.1946	0.1670	0.2113	8.4261	86	3	89
TSC	-0.1971	0.0100	0.2071	7.5759	90	4	76
TCH	-0.1805	0.0270	0.2075	8.8501	92	5	79
ETU	-0.2183	0.0031	0.2214	7.8619	93	6	72
TMTU	-0.1894	0.0131	0.2025	9.9153	94	7	59
MPMU					94	8	67
BPMU					80	9	42

[a] Ref [9,29]

The nonlinear equation has been derived from the linear model, which approximates the corrosion inhibitor efficiency (E_{cal} %) is:

$$IE_{cal}\% = Ax_iC_i + B \qquad (11)$$

where A and B are constants obtained by regression analysis, x_j is a quantum chemical index characteristic for the molecule, and C_i denotes the experiments concentration. Equation 10 was used to derive the next equation, which is the non-linear model (NML) proposed by Lukovits and coworker[30] for studying the interaction of corrosion inhibitors with metal surfaces in acidic medium.

$$IE\% = \frac{(Ax_iC_i + B)C_i}{1 + (Ax_iC_i + B)C_i} \times 100 \qquad (12)$$

In the non-linear method of analysis, multiple regressions were performed on inhibition efficiencies of seven derivatives of thiourea by using data of TABLE 4. This equation obtained in SigmaPlot 11 software[31] as follows with $R^2=0.8280$ and $S=0.072$,

$$IE\% = \frac{(-2.9719E_{HOMO} + 29.0911E_{LUMO} + 0.0989\mu) \times C_i}{1 + (-2.9719E_{HOMO} + 29.0911E_{LUMO}) \times C_i} \times 100 \qquad (13)$$

Figure 2 shows the correlation between experimental and calculated inhibition efficiency obtained from Eq (13) for seven substituted thiourea compounds. By using this relationship and the data from TABLE 1, the inhibition efficiencies of the titled compounds were calculated and listed in TABLE 4. According to the results of the reported experimental efficiencies for the seven derivatives of thiourea compounds, they show that amino, methyl and ethyl substitutions increase the thioamid group activities as inhibitor, and the number of them causes to increase this phenomena considerably, and ethyl substitution is more than amino and methyl, 93%, 90% and 86%. MPMU and BPMU have 94% and 80% In the titled compounds, the peridinium methyl substitution decreases the activity of the thiourea but the substituted methyl on different position, either on chain or peridinium ring, increases the inhibition property of the base compound, 1, and the substituted fluorine decreases this behaviour. The substituted methyl on the R3 position has the highest effect on the inhibition efficiency, and the substituted fluorine on the R4 position has the violent decreasing effect on the efficiency.

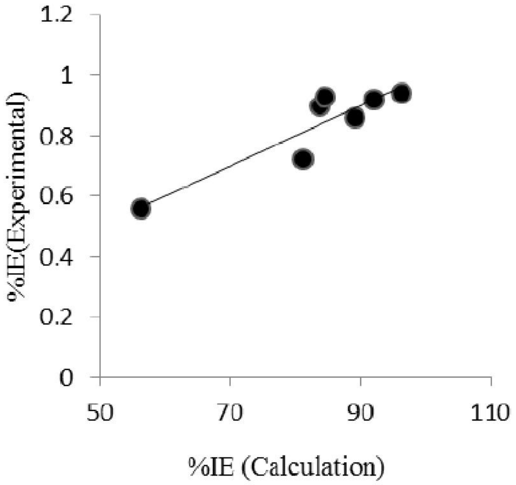
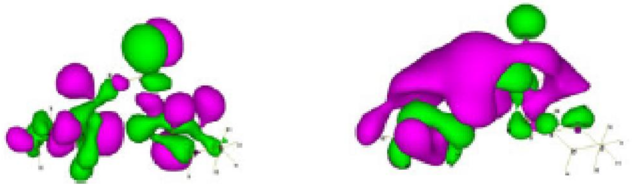


Figure 2 : Correlation between experimental inhibition efficiency and calculated inhibition efficiency obtained from B3LYP/6-31G for seven substituted thiourea compounds**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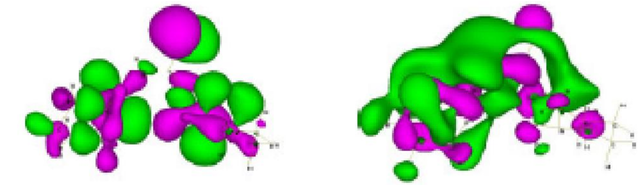
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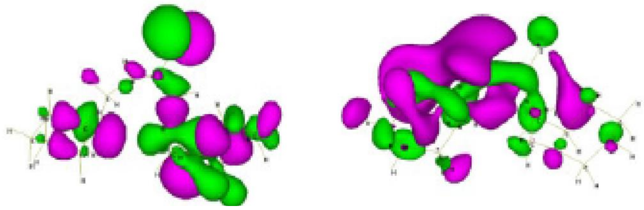
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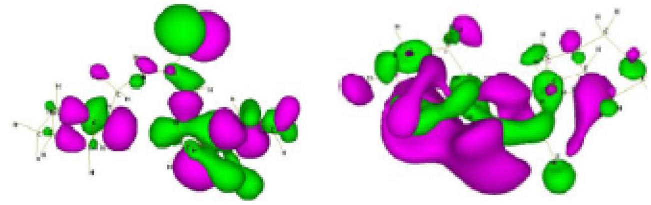
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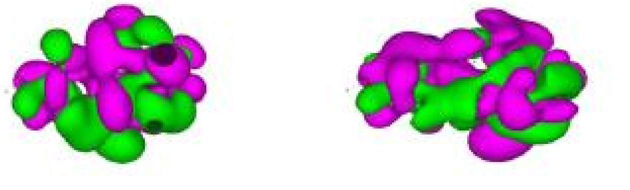
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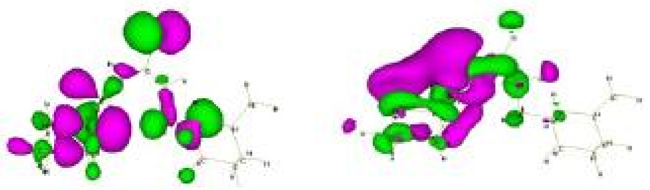
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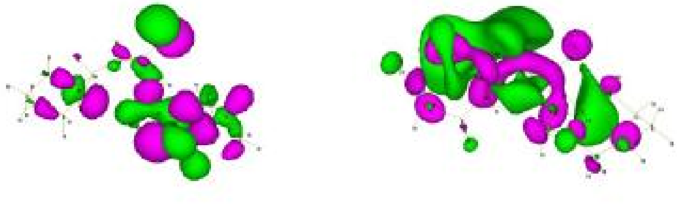
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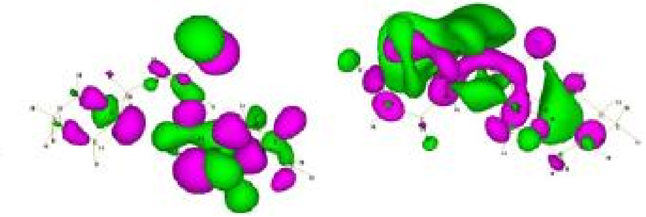
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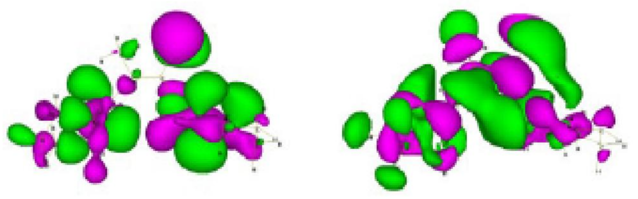
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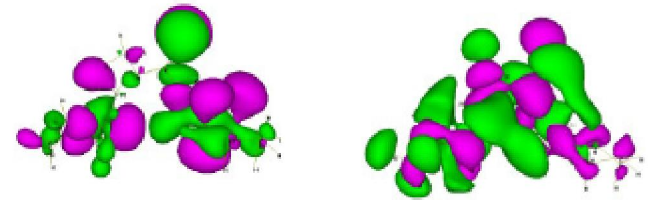
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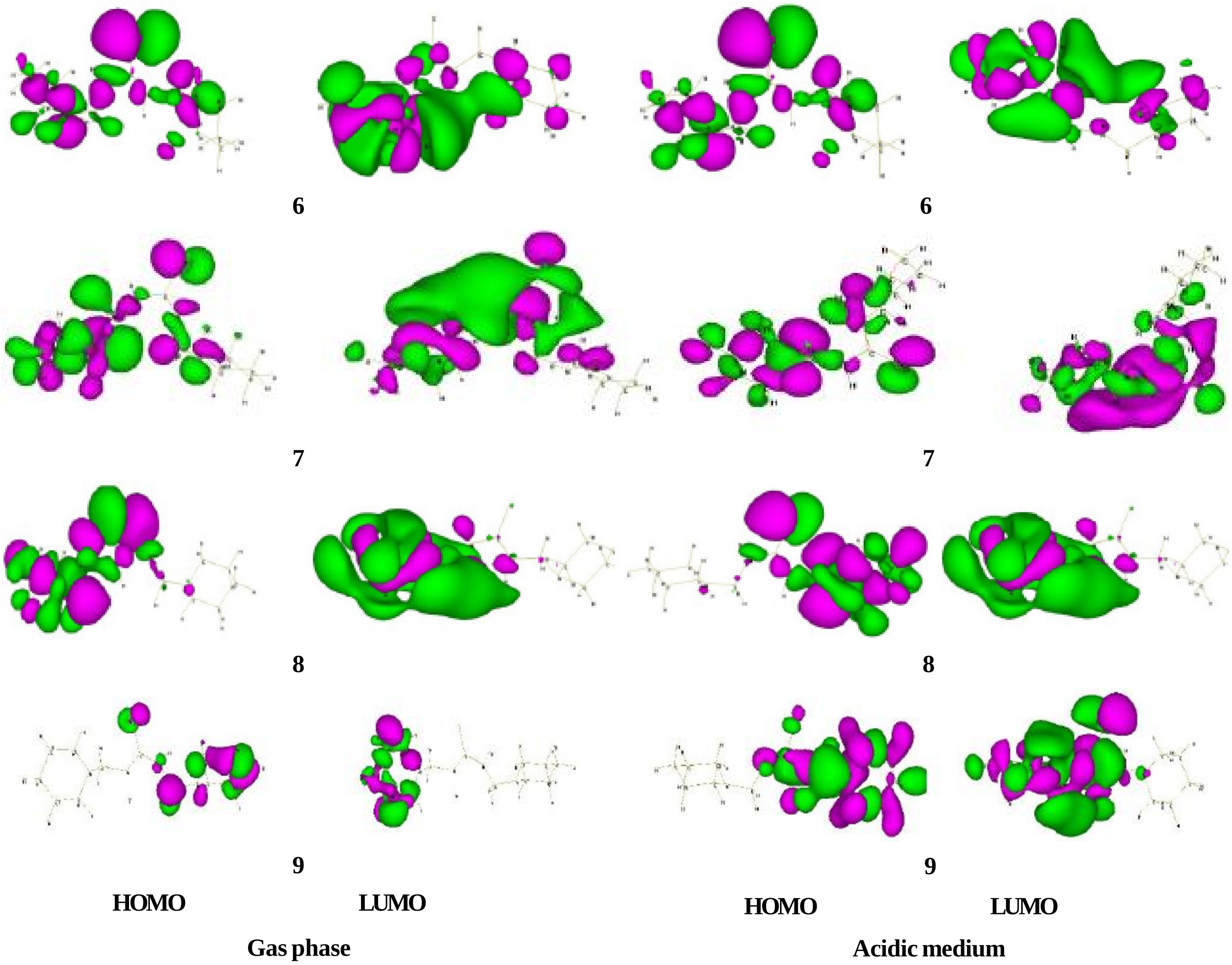

Figure 3 : Localization of HOMO and LUMO orbital's in the gas and liquid phase for the compounds 1-9

Frontier orbital's electron densities

Frontier orbital's electron densities on atoms provide a useful means for the detailed characterization of donor-acceptor interaction. In Figure 3, there is a representation of the HOMO and LUMO orbital's calculated in both gas phase and acidic medium. In both phases, HOMO and LUMO are located on both regions, especially on S and N atoms. The compounds 3 and 9 are exceptional cases. HOMOs and LUMOs are located on thiocarbonyl group and substituted peridinium methyl, respectively. In the compound 3, which has highest inhibition efficiency compared to others, HOMO and LUMO are located on the whole molecule in the gas phase, but on substituted predinium methyl in the acidic phase. The solvent increases the localization of the frontier orbitals in the compound 9.

CONCLUSIONS

A theoretical investigation in order to know the behaviour of reactive sites in bis-piperidiniummethyl-thiourea and seven its derivatives as corrosion inhibitors, by using the B3LYP/6-31G** at the level of theory has been performed. Considering the Fukui functions, Dual descriptor and a Mulliken population analysis in the gas phase, we concluded that the reactive sites of these derivatives are located mainly on the nitrogen and sulphur atoms which are the most susceptible site for an electrophilic attack. We also obtained an equation to predict the inhibition efficiency of these compounds. On the basis of the analysis of the obtained results, and the location of the HOMO, it can be concluded that the compounds 1, 5 are those that present the greater potential for their use as possible corrosion inhibitors. As far as the geometries, the results indicated that in the gaseous and liquid phase, the structures were similar. The quantum chemical calculations indicated that considering only one parameter is not suitable, hence several parameters or a composite index of more than two or more quantum chemical parameters were taken into consideration to characterize the inhibition activity of the molecules. By means of the calculation of parameters as E_{HOMO}, E_{LUMO}, μ, we concluded that derivatives of bis-piperidiniumemethyle-thiourea with electron-donating substituent have higher efficiency than molecule without substitution or compound of electron withdrawing group.

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