Research Article

Quantum Chemical Study of Some Antihistamines as Inhibitors Corrosion for Copper in Nitric Acid Solution Using DFT Method

M. A. Tigori[1]*, A. Kouyate[1], V. Kouakou[2], P. M. Niamien[2] and A. Trokourey[2]

[1]UFR Environnement, Université Jean Lorougnon Guédé, BP 150 Daloa, Côte d'Ivoire
[2]Laboratoire de Chimie Physique, Université Félix Houphouët Boigny, 22 BP 582 Abidjan 22, Côte d'Ivoire

Abstract

In this work three antihistamines namely 4-(8-chloro-5,6-dihydro-11H-benzo [5,6] cyclohepta [1,2-b] pyridin-11-ylidene)-1-piperidinecarboxylic acid ethyl ester or loratadine; 8-chloro-11-[1-[(5-methyl-3-pyridil)methyl] piperidin-4-ylidene]-6,11-dihydro-5H-benzo-[5,6] cyclohepta [1,2-b] pyridine or rupatadine and 2-[(1-[1-(4-fluorobenzul)-1H-benzimidazol-2-yl]-4-piperidinyl)(methyl)amino-4(3H) pyrimidinone or mizolastine have been theoretically studied using density functional theory (DFT) at the B3LYP/6-31G(d) level in order to show their inhibition properties in the copper corrosion. Quantum chemical parameters such as E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap (ΔE), dipole moment (μ), electronegativity (χ) hardness (η), softness (S), electrophylicity indexη (ω), electron affinity (A), ionization energy (I) and the fraction of electron transferred (ΔN) have been calculated and discussed. The local parameters as the Fukui function and condensed softness were analysed. This leads to a better understanding of the mechanism of corrosion inhibition. The results revealed that all inhibit corrosion and their inhibition efficiencies follow the order : mizolastine > loratadine > rupatadine.

Keywords: Antihistamines, Inhibition properties, Acid nitric solution, Copper, DFT

***Correspondence**
Author: M. A. Tigori
Email: tigori20@yahoo.fr

Introduction

Corrosion is a constant problem in metal systems; it occurs in households as well as in transport, agriculture and industry. Corrosion often leads to accidents, contamination and malfunctions in electrical and electronic systems. This phenomenon, which results from the physicochemical interactions between the metal and its environment, leads to the degradation of the metal.

Copper is one of the metals with a wide range of applications because of its mechanical, thermal and electrical conductivity. It is resistant to the atmosphere and many chemicals. However, acid solutions, widely used [1, 2] in industry for pickling or cleaning, stimulating oil wells, removing deposits and industrial synthesis cause its dissolution. To slow down the dissolution of metals, the use of corrosion inhibitors is a solution. To protect the environment, the choice of eco-friendly and biodegradable corrosion inhibitors is becoming an important issue [3]. This is why several studies in the literature have focused on the action of certain therapeutic molecules on metal corrosion. Thus, molecules such as antibiotics [4-6], antifungals [7, 8], vitamins [9, 10], muscle relaxants [11, 12]. So, organic compounds containing nitrogen, oxygen and sulphur, are the most common effective and economic method to protect metal corrosion [13]. Theoretical chemistry has been used recently to explain the mechanism of corrosion inhibition, such as quantum chemical calculations [14–16]. They are very helpful in understanding the relationship between the corrosion the structural and inhibition properties of a wide range of organic corrosion inhibitors [17, 18]. The objective of the present work is to investigate the inhibition properties of three compounds; loratadine, rupatadine and mizolastine on theoretical parameters such as global parameters and local parameters based on the Fukui indices indicated the possible sites for nucleophilic and electrophilic attacks. Using density functional theory (DFT) method which has provided very useful framework for developing new criteria for rationalizing predicting, and eventually understanding many aspect of chemical processes [19]. The chemical structures of compounds studied are given in **Figure 1**.

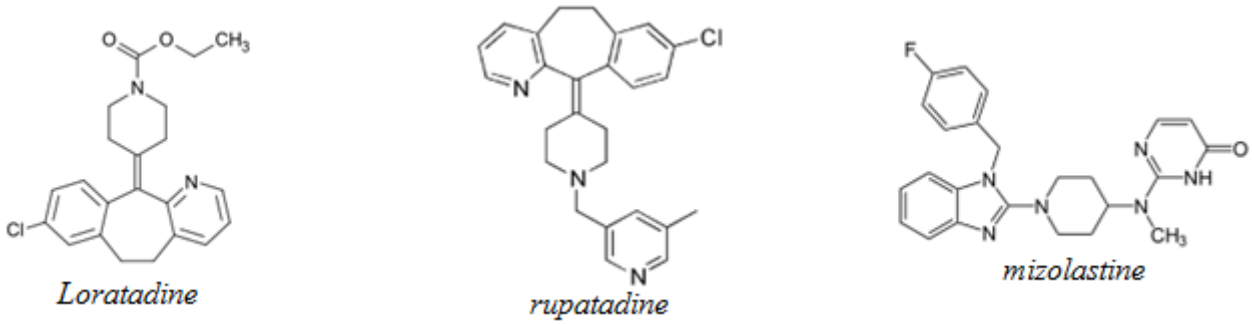

Figure 1 The molecular structures

Computational Methodology

DFT Method

DFT (Density Functional Theory) method is used to calculate theoretical parameter which permitted to explain inhibition properties of molecules. Furthermore, DFT is considered a very useful technique to probe the inhibitor / surface interaction as well as to analyze the experimental data. In this work the calculations were performed using the hybrid functional B3LYP, a version of DFT using Becke's three parameter exchange terms associated with the gradient corrected correlation functional of Lee, Yang, and Parr (LYP) [20]. The full geometry optimization in **Figure 2** was carried out at B3LYP/6-31G(d) level of theory, using Gaussian 09W [21].

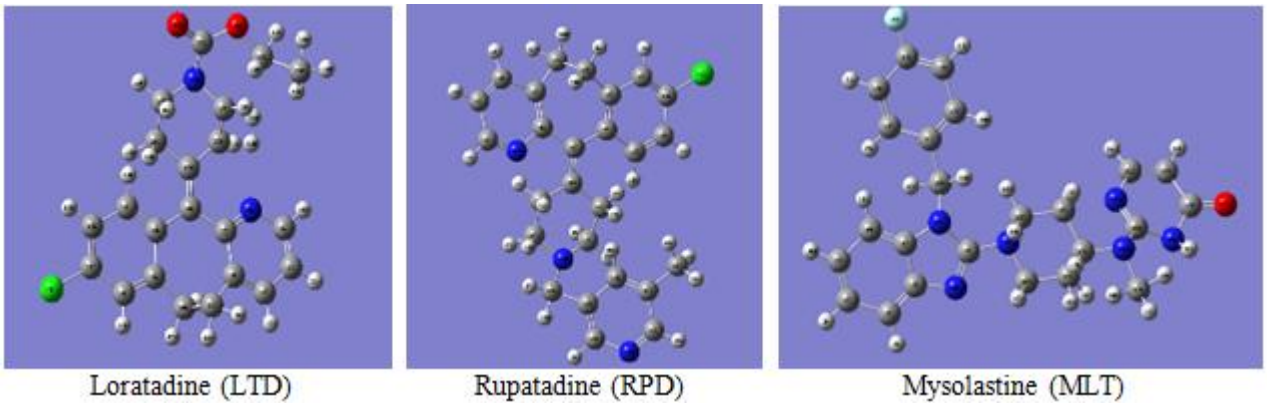

Figure 2 Optimized structure of LTD, RPD and MLT by B3LYP/6-31G(d)

Global parameters

According to Koopmans' theorem [22], the ionization (I) and electron affinity (A) of the molecules are calculated using the following equations.

$$I = -E_{HOMO} \qquad (1)$$

$$A = -E_{LUMO} \qquad (2)$$

The electronegativity (χ) and the global hardness (η) of the inhibitors were estimated using the value of I and A [24] that given by:

$$\chi = \frac{I+A}{2} = -\frac{E_{LUMO}+E_{HOMO}}{2} \qquad (3)$$

$$\eta = \frac{I-A}{2} = \frac{E_{LUMO}-E_{HOMO}}{2} \qquad (4)$$

The global softness S is the inverse of global hardness [23], it measure of the capacity of an atom or group of atoms to receive electrons. It is estimated by the above equation:

$$S = \frac{1}{\eta} = \frac{2}{I-A} \quad (5)$$

The global electrophilicity index was introduced by Parr [24] as a measure of energy lowering owing to maximal electron flow between donor and acceptor and ω is defined as follows:

$$\omega = \frac{\mu_P^2}{2\eta} \quad (6)$$

According to Pearson theory [25] the fraction of transferred electrons (ΔN) from the inhibitor molecule to the metallic atom can be calculated using the equation below:

$$\Delta N = \frac{\chi Cu - \chi inh}{2(\eta_{Cu} + \eta_{inh})} \quad (7)$$

Where χ_{Cu} and η_{Cu}, χ_{inh} and η_{inh} denote the electronegativity and hardness of copper and the inhibitor molecule respectively.

We use the theoretical value of χ_{Cu}= 4.98 *eV/m* and η_{Cu}= 0 [25], for the calculation of the number of transferred electrons.

Local parameters

The local reactivity is analyzed by the local parameters that are based in general on the Fukui functions proposed by Parr and Yang [26]. Their values are used to identify which atoms in the inhibitor are more prone to undergo an electrophilic or nucleophilic attack. The Fukui function is defined as the first derivative of the electronic density $\rho(r)$ of a system with respect to the number of electrons N at a constant external potential $v(r)$ [27].

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} = \left(\frac{\delta \mu_P}{\partial v(r)}\right)_N \quad (8)$$

The change in electron density is the nucleophilic $f^+(r)$ and electrophilic $f^-(r)$ Fukui functions, which can be calculated using the finite difference approximation as follows [27] :

- nucleophilic attack $f^+(r) = \rho_{N+1}(r) - \rho_N(r) \approx \rho_{BV}$ (9)
- electrophilic attack $f^-(r) = \rho_N(r) - \rho_{N-1}(r) \approx \rho_{HO}$ (10)

Where (r) is the electron density at a point r in the space around the molecule. N is the number of electrons in the neutral species, when (N + 1) corresponds to an anion with an electron added to the LUMO of the molecule and (N - 1) is the cation with an electron removed from the HOMO the molecule.

In order to use these functions is often, it is necessary to condense the atom variant are written for the atomic site k of the molecule. Under these conditions, the corresponding Fukui functions [28] are expressed by replacing the associated electron densities by respective electron population q_k as:

- nucleophilic attack $f_k^+ = q_k(N+1) - q_k(N)$ (11)
- electrophilic attack $f_k^- = q_k(N) - q_k(N-1)$ (12)

Where $q_k(N+1)$, $q_k(N)$ and $q_k(N-1)$ are the electronic population of atom k in $(N+1)$, N and $(N-1)$ electrons systems. Condensed softness [29] indices of reactivity can be estimated as follows:

$$s_k^\alpha(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)}^{\alpha} \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} = f_k^\alpha(r) S \quad (13)$$

Where $\alpha = 1$ or -1 for nucleophilic and electrophilic attack, respectively.

Results and Discussion

Global reactivity

Quantum chemical parameters are obtained from calculations, which make it possible to study the inhibition properties of molecules. They are recorded in the **Table 1**.

Table 1 Quantum chemical descriptors for inhibitor LTD, RPD and MLT calculated using B3LYP/6-31G(d)

Parameters	LTD	RPD	MLT
E_{HOMO} (eV)	-5.6660	-5.8978	-5.2545
E_{LUMO} (eV)	-1.6910	-1.0559	-1.8352
Energy gap ΔE (eV)	3.9750	4.8419	3.4193
Dipole moment $\mu\ (D)$	8.1898	7.5116	4.9876
Ionization energy $I(eV)$	5.6660	5.8978	5.2545
Electron affinity $A(eV)$	1.6910	1.0559	1.8352
Electronegativity $\chi\ (eV)$	3.6785	3.4767	3.5449
Hardness $\eta\ (eV)$	1,988	2.4209	1.7097
Softness $(S(eV)^{-1}$	0.5031	0.4131	0.5849
Fraction of electron transferred ΔN	0.3274	0.3111	0.4197
Electrophylicity index ω	3.4041	2.4921	3.6751
Total energy $E_T(au)$	-1572.15	-1630.8	-1432.38

The frontier molecular orbital (FMO) theory of chemical reactivity [30], transition of electron is due to interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species. The high value of E_{HOMO} (highest occupied molecular orbital energy) of the molecule shows its tendency to donate electrons to unoccupied d orbital of the metal surface. Thus, translating the adsorption phenomenon which is marked by the transport of electrons, reinforces the adsorbed surface of the copper, and therefore enhances the inhibition efficiency. According to the values of E_{HOMO} in Table 1, it is observed that E_{HOMO} increases in the following order: MLT > LTD > RPD. In our case the highest value E_{HOMO} -5.2545 eV of MLT indicates the better inhibition efficiency. In addition, the lower value of E_{LUMO}, the easier the acceptance of electrons from metal surface. In the table 1 MLT has the lowest value of E_{LUMO}, so it has the greatest ability to interact with the metal surface what mean MLT would preferentially accept more electrons from metal surface than the other inhibitors LTD and RPD.

The energy gap $(\Delta E = E_{LUMO} - E_{HOMO})$ is an important reactivity parameter of the inhibitor molecule towards the adsorption on the metallic surface. So, low value of ΔE indicates better adsorption and higher inhibition efficiency [31]. Indeed the high values of ΔE reflect a high electronic stability and a low reactivity of the molecule. The low values of ΔE indicate that it will be easier to remove an electron from the HOMO orbital to LUMO one which can result in good inhibition. In this study the inhibitor MLT has the lowest energy gap 3.4193 eV Compared to LTD and RPD inhibitors which have energy gap of 3.9750 eV and 4.8419 eV respectively. It means that MLT could be the best corrosion inhibitor.

The dipole moment (μ) is a parameter used to describe the polarity of a covalent bond resulting from a non-uniform distribution of charges on the different atoms of the molecule. Adsorption between the inhibitor and the metal surface can be favoured by a high value of the dipole moment [32, 33]. However, many other authors [34, 35] state that low values of the dipole moment favour the adsorption process. In our case the dipole moments of LTD and RPD molecules are high while that of MLT is low. In spite of these inconsistent viewpoints there is no significant relationship between dipole moment and inhibition efficiency.

Ionization energy (I) is a parameter that explains the chemical reactivity of atoms and molecules, since a high ionization energy indicates that the molecule is stable and inert to any chemical reaction, while a low ionization energy indicates a high reactivity of atoms and molecules [36]. The low ionization energy (5.2545 eV) of MLT indicates the high inhibition efficiency. Otherwise the high value of Electron affinity (A) when compared to values in the literature [37, 38], indicate the capacity of the molecules to accept electrons.

The electronegativity (χ) of a molecule is a chemical quantity that characterizes its ability to attract electrons to itself through a covalent bond. According to Sanderson's principle of electronegativity equalization [39], the molecule with high electronegativity has a low reactivity, which indicates low inhibition efficiency. In our case, the three molecules have a low electronegativity and therefore have good inhibition efficiency.

Global softness (S) and global hardness (η) are also important reactivity parameters that provide information on the likely ability of a molecule to interact with a metal surface. So hard molecule has a large energy gap and a soft molecule has a small energy gap [40]. In general soft molecules are more reactive than hard molecules. It means a

molecule has a low value of global hardness and a high value of global softness is expected to be a good inhibitor. It is shown from the calculations that MLT has the least value of global hardness (1.7097 eV) and the highest value of global softness (0.5849 eV) could be having the highest inhibition efficiency.

The fraction of electrons transferred (ΔN) was also calculated. If ΔN < 3.6 [41], it is an indicator of the tendency of a molecule to donate electrons to the metal. In our study, the fraction of electrons transferred of the molecules are less than 3.6; this reflects all molecules owe their inhibition properties to the transfer of electrons from these molecules to metal. The obtained values of ΔN reported in Table 1 show that MLT have the highest value (0.4197) which implies good possibility of MLT to donate its electrons to the cooper when compared to LTD and RPD who have the lowest value respectively 0.3274 and 0.3111. Indeed, good inhibitors are generally molecules that are able to give electrons to the metal surface. That means MLT has high inhibition efficiency.

The electrophilicity index (ω) is a parameter that describes the nucleophilic and electrophilic nature of a molecule. A high value of the electrophilicity index describes a good electrophile while a low value of the electrophilicity index describes a good nucleophile [42]. In this study the electrophilicity index values of the different molecules are high, which shows that these molecules are good electrophiles. They have the ability to accept electrons from copper.

For the three molecules, $\eta > 0$ and $E_T < 0$, the charge transfer from each molecule to the metal is energetically favored [43].

Local reactivity

The local reactivity of molecule LTD, RPD and MLT is analyzed by means of the condensed Fukui function. The condensed Fukui function and local softness indices are able to correctly predict the site reactivity (most probable nucleophilic or electrophilic attack site). The charges of the atoms, condensed Fukui functions and softness indices of molecule LTD, RPD and MLT are tabulated respectively in **Table 2-4**.

The local reactivity of a molecule is explained by the Fukui functions [44]; these help to rationalize the reactivity of individual molecular orbital contributions. The distinction of each part of the molecule on the basis of its distinct chemical behaviour due to the different substituted functional groups is explained by the condensed Fukui function and local softness indices. The preferred site for nucleophilic attack is the atom in the molecule where the value of f_k^+ or s_k^+ is maximum and is associated with LUMO energy, while the site for electrophilic attack is controlled by the values of f_k^- or s_k^- which is associated with HOMO energy. On the other hand f_k^+ measures the changes of density when the molecule gains electrons f_k^- corresponds to reactivity when the molecule loss electrons.

In Table 2, for LTD the probable nucleophilic attack centre is N(22) and that of probable electrophilic attack is C(33). In that concerns RPD, Table 3 the atom C(6) is the preferred site for nucleophilic attack, as this site has the highest value of f_k^+; the atom C(11) is the preferred site for electrophilic attack since this atom has the highest value of f_k^-. The results of MLT reported in Table 4 reveal that most probable site for nucleophilic attack is N(49) and the electrophilic attack is C(2). The HOMO and LUMO orbitals of each molecule are given in **Figure 3**.

Corrosion inhibition mechanism

The fraction of electron transferred $(\Delta N)$and the electrophilicity index(ω) obtained in our study suggest a physical barrier consisting of a complex obtained by electron transferred from the most probable center for electrophilic attacks (center for which the value of the f_k^- is maximum belonging to the HOMO zone) to the incomplete orbitals of the ions Cu^{2+}:

$$Ath \rightarrow Cu^{2+}[Cu - Ath] \qquad (14)$$

The molecules could receive electrons from the orbitals (d) of copper at the most probable center for nucleophilic attack (center for which the value of the f_k^+ maximum belonging to the LUMO zone) which would strengthen the link between the metal and the molecule.

$$Ath \leftarrow Cu^{2+}[Cu - Ath] \qquad (15)$$

These electron transfers justify the existence of the phenomenon of chemisorption which is predominant in the process of adsorption of molecules on the surface of copper (**Figure 4**).

In addition, in a nitric acid solution some molecules are protonated:

$$Ath + H^+ \rightleftarrows [AthH]^+ \qquad (16)$$

The interactions between the protonated species and the ions NO_3^- adsorbed on the surface of the metal certainly justify the existence of physisorption.

Table 2 Fukui and local softness indices for nucleophilic and electrophilic attacks for the atoms of LTD calculated using Mulliken charges

Atom	$q_k(N+1)$	$q_k(N)$	$q_k(N-1)$	f_k^+	f_k^-	s_k^+	s_k^-
1 C	0.003745	0.026275	-0.007247	-0.02253	0.033522	-0.01133484	0.01686492
2 C	0.002679	0.282502	0.000196	-0.279823	0.282306	-0.14077895	0.14202815
3 C	-0.008461	-0.02058	0.001289	0.012119	-0.021869	0.00609707	-0.01100229
4 C	0.006635	-0.184788	0.00108	0.191423	-0.185868	0.09630491	-0.09351019
5 C	-0.004369	-0.131138	0.013507	0.126769	-0.144645	0.06377748	-0.0727709
6 C	-0.01177	0.063734	0.032178	-0.075504	0.031556	-0.03798606	0.01587582
7 C	0.001989	0.232612	0.007232	-0.230623	0.22538	-0.11602643	0.11338868
8 C	0.002934	0.114453	-0.009328	-0.111519	0.123781	-0.05610521	0.06227422
9 C	-0.006642	-0.188826	0.015887	0.182184	-0.204713	0.09165677	-0.10299111
10 H	0.000364	-0.021255	-0.000798	0.021619	-0.020457	0.01087652	-0.01029192
11 C	0.002271	-0.161522	-0.00541	0.163793	-0.156112	0.08240426	-0.07853995
12 C	-0.002773	-0.057349	0.012639	0.054576	-0.069988	0.02745719	-0.03521096
13 C	-0.002031	-0.220257	-0.006179	0.218226	-0.214078	0.1097895	-0.10770264
14 H	-0.000146	0.151953	0.000254	-0.152099	0.151699	-0.07652101	0.07631977
15 H	-0.00031	0.14141	-0.000161	-0.14172	0.141571	-0.07129933	0.07122437
16 H	0.000031	0.141108	-0.000708	-0.141077	0.141816	-0.07097584	0.07134763
17 H	-0.000071	0.153145	0.000187	-0.153216	0.152958	-0.07708297	0.07695317
18 H	0.000103	0.145566	0.000234	-0.145463	0.145332	-0.07318244	0.07311653
19 Cl	-0.000441	0.017865	0.000374	-0.018306	0.017491	-0.00920975	0.00879972
20 C	-0.002754	0.436864	0.001444	-0.439618	0.43542	-0.22117182	0.2190598
21 C	-0.055879	-0.494088	0.001313	0.438209	-0.495401	0.22046295	-0.24923624
22 N	-0.008461	-0.524296	0.020398	**0.515835**	-0.544694	**0.25951659**	-0.27403555
23 C	-0.026158	-0.103261	-0.062305	0.077103	-0.040956	0.03879052	-0.02060496
24 C	-0.000152	-0.138598	-0.002268	0.138446	-0.13633	0.06965218	-0.06858762
25 C	-0.002883	-0.399519	0.001789	0.396636	-0.401308	0.19954757	-0.20189805
26 C	0.004788	0.048154	0.011088	-0.043366	0.037066	-0.02181743	0.0186479
27 C	-0.027551	-0.02235	0.046287	-0.005201	-0.068637	-0.00261662	-0.03453127
28 H	0.00262	0.180897	-0.007621	-0.178277	0.188518	-0.08969116	0.09484341
29 H	0.000082	0.194109	-0.000229	-0.194027	0.194338	-0.09761498	0.09777145
30 H	0.000341	0.249517	-0.000305	-0.249176	0.249822	-0.12536045	0.12568545
31 H	0.000388	0.216198	0.000445	-0.21581	0.215753	-0.10857401	0.10854533
32 N	-0.008258	-0.439756	0.016783	0.431498	-0.456539	0.21708664	-0.22968477
33 C	-0.000505	0.705978	-0.004619	-0.706483	**0.710597**	-0.3554316	**0.35750135**
34 O	0.022458	-0.48855	0.000568	0.511008	-0.489118	0.25708812	-0.24607527
35 O	0.057675	-0.447804	0.059526	0.505479	-0.50733	0.25430648	-0.25523772
36 C	0.035209	-0.215306	0.347087	0.250515	-0.562393	0.1260341	-0.28293992
37 C	-0.816454	-0.681679	0.55412	-0.134775	-1.235799	-0.0678053	-0.62173048
38 H	-0.06158	0.241781	-0.015268	-0.303361	0.257049	-0.15262092	0.12932135
39 H	-0.020701	0.14662	-0.01502	-0.167321	0.16164	-0.0841792	0.08132108
40 H	-0.012779	0.258506	-0.008916	-0.271285	0.267422	-0.13648348	0.13454001
41 H	0.081322	0.125982	-0.022078	-0.04466	0.14806	-0.02246845	0.07448899
42 H	0.023377	0.23451	0.008146	-0.211133	0.226364	-0.10622101	0.11388373
43 H	-0.00074	0.178886	0.001424	-0.179626	0.177462	-0.09036984	0.08928113
44 H	0.000028	0.264302	0.000784	-0.264274	0.263518	-0.13295625	0.13257591
45 H	0.008581	0.079473	-0.010271	-0.070892	0.089744	-0.03566577	0.04515021
46 H	-0.008066	0.082411	0.019195	-0.090477	0.063216	-0.04551898	0.03180397
47 H	0.000101	0.171681	-0.000055	-0.17158	0.171736	-0.0863219	0.08640038

48 H	0.001079	0.190737	-0.000062	-0.189658	0.190799	-0.09541694	0.09599098
49 H	-0.002527	0.2863	0.001165	-0.288827	0.285135	-0.14530886	0.14345142
50 H	-0.001633	0.266739	0.002226	-0.268372	0.264513	-0.13501795	0.13307649

Table 3 Fukui and local softness indices for nucleophilic and electrophilic attacks for the atoms of RPD calculated using Mulliken charges.

Atom	$q_k(N+1)$	$q_k(N)$	$q_k(N-1)$	f_k^+	f_k^-	s_k^+	s_k^-
1 C	-0.127482	-0.133662	-0.142078	0.00618	0.008416	0.00255234	0.00347665
2 C	-0.13489	-0.143154	-0.15643	0.008264	0.013276	0.00341303	0.00548432
3 C	-0.034972	-0.038707	-0.036993	0.003735	-0.001714	0.00154256	-0.00070805
4 C	0.159672	0.151505	0.135951	0.008167	0.015554	0.00337297	0.00642536
5 C	0.096944	0.087894	0.063457	0.00905	0.024437	0.00373765	0.01009492
6 C	-0.113756	-0.243601	-0.20762	**0.129845**	-0.035981	**0.05362599**	-0.01486375
7 C	0.053121	0.048898	0.033345	0.004223	0.015553	0.0017441	0.00642494
8 C	0.134734	0.136822	0.134103	-0.002088	0.002719	-0.00086234	0.00112322
9 C	-0.11301	-0.119818	-0.12771	0.006808	0.007892	0.0028117	0.00326019
10 H	0.164035	0.143945	0.125044	0.02009	0.018901	0.00829717	0.007808
11 C	0.284136	0.259697	0.154294	0.024439	**0.105403**	0.01009331	**0.04354198**
12 C	-0.143985	-0.150571	-0.16491	0.006586	0.014339	0.00272002	0.00592344
13 C	-0.063385	-0.061284	-0.062136	-0.002101	0.000852	-0.00086771	0.00035196
14 H	0.163395	0.134706	0.088415	0.028689	0.046291	0.01184856	0.01912281
15 H	0.167059	0.142478	0.10774	0.024581	0.034738	0.01015195	0.01435027
16 H	0.166159	0.146552	0.106178	0.019607	0.040374	0.00809769	0.0166785
17 H	0.158788	0.146869	0.121448	0.011919	0.025421	0.00492255	0.01050142
18 H	0.085677	0.098382	0.093191	-0.012705	0.005191	-0.00524717	0.0021444
19 C	-0.296639	-0.295287	-0.287104	-0.001352	-0.008183	-0.00055838	-0.0033804
20 C	0.06252	0.075345	0.06595	-0.012825	0.009395	-0.00529673	0.00388107
21 C	-0.312411	-0.313166	-0.307217	0.000755	-0.005949	0.00031182	-0.00245753
22 C	-0.283196	-0.257491	-0.243475	-0.025705	-0.014016	-0.01061617	-0.00579001
23 C	-0.216593	-0.17098	-0.154478	-0.045613	-0.016502	-0.01883817	-0.00681698
24 H	0.295285	0.273121	0.265638	0.022164	0.007483	0.00915373	0.00309123
25 H	0.21793	0.19876	0.180582	0.01917	0.018178	0.00791721	0.00750933
26 H	0.253102	0.234284	0.214509	0.018818	0.019775	0.00777183	0.00816905
27 H	0.18462	0.138765	0.110042	0.045855	0.028723	0.01893812	0.01186547
28 C	0.033704	0.016728	0.016488	0.016976	0.00024	0.00701109	0.000099144
29 C	0.025483	0.030153	0.039311	-0.00467	-0.009158	-0.00192871	-0.00378317
30 C	-0.097907	-0.11065	-0.116806	0.012743	0.006156	0.00526286	0.00254304
31 C	0.055231	0.055803	0.050957	-0.000572	0.004846	-0.00023624	0.00200188
32 C	0.056153	0.012964	-0.008295	0.043189	0.021259	0.01783706	0.00878209
33 C	-0.030106	-0.08113	-0.098371	0.051024	0.017241	0.02107291	0.00712226
34 H	0.06996	0.053914	0.044024	0.016046	0.00989	0.006627	0.00408556
35 H	0.188338	0.127314	0.086926	0.061024	0.040388	0.02520291	0.01668428
36 H	0.174282	0.122725	0.09117	0.051557	0.031555	0.02129304	0.01303537
37 C	-0.313131	-0.323147	-0.284857	0.010016	-0.03829	0.00413661	-0.0158176
38 C	-0.498274	-0.493629	-0.463027	-0.004645	-0.030602	-0.00191839	-0.01264169
39 N	-0.583403	-0.56684	-0.573149	-0.016563	0.006309	-0.00684052	0.00260625
40 N	-0.465112	-0.511266	-0.504576	0.046154	-0.00669	0.0190616	-0.00276364
41 N	-0.364677	-0.399776	-0.427403	0.035099	0.027627	0.01449589	0.01141271
42 Cl	0.149223	0.105493	0.051464	0.04373	0.054029	0.01806049	0.02231938
43 H	0.178006	0.157583	0.132292	0.020423	0.025291	0.0084347	0.01044771
44 H	0.222319	0.187558	0.16834	0.034761	0.019218	0.01435629	0.00793896
45 H	0.192336	0.139929	0.110273	0.052407	0.029656	0.02164409	0.01225089
46 H	0.233638	0.217636	0.206054	0.016002	0.011582	0.00660883	0.00478452
47 H	0.244087	0.2121	0.121625	0.031987	0.090475	0.01321063	0.03737522
48 H	0.295556	0.260858	0.165493	0.034698	0.095365	0.01433027	0.03939528
49 H	0.247625	0.227318	0.136667	0.020307	0.090651	0.00838679	0.03744793
50 H	-0.254486	-0.254615	-0.254274	0.000129	-0.000341	0.00053277	-0.00014087

51 H	0.208852	0.198545	0.166654	0.010307	0.031891	0.00425679	0.01317417
52 H	0.188066	0.166051	0.122299	0.022015	0.043752	0.0090922	0.01807395
53 C	-0.486464	-0.489259	-0.489996	0.002795	0.000737	0.00115434	0.00030445
54 H	0.180062	0.15197	0.133871	0.028092	0.018099	0.011602	0.0074767
55 H	0.159767	0.141275	0.137484	0.018492	0.003791	0.0076372	0.00156606
56 H	0.184017	0.154094	0.129627	0.029923	0.024467	0.0123582	0.01010732

Table 4 Fukui and local softness indices for nucleophilic and electrophilic attacks for the atoms of MLT calculated using Mulliken charges

Atom	$q_k(N+1)$	$q_k(N)$	$q_k(N-1)$	f_k^+	f_k^-	s_k^+	s_k^-
1 C	0.267428	0.236487	0.222164	0.030941	0.014323	0.01809739	0.00837752
2 C	0.552195	0.555615	0.502305	-0.00342	**0.05331**	-0.00200036	**0.03118102**
3 C	-0.193977	-0.231912	-0.2623	0.037935	0.030388	0.02218818	0.01777394
4 C	-0.127061	-0.138493	-0.140295	0.011432	0.001802	0.00668658	0.00105399
5 C	-0.120128	-0.14497	-0.160081	0.024842	0.015111	0.01453009	0.00883842
6 C	-0.257359	-0.28421	-0.281548	0.026851	-0.002662	0.01570515	-0.001557
7 C	0.305556	0.296548	0.290684	0.009008	0.005864	0.00526878	0.00342985
8 H	0.206132	0.147175	0.108281	0.058957	0.038894	0.03448395	0.0227491
9 H	0.198657	0.13331	0.095394	0.065347	0.037916	0.03822146	0.02217707
10 H	0.189444	0.135641	0.101832	0.053803	0.033809	0.03146937	0.01977488
11 H	0.283662	0.256469	0.237872	0.027193	0.018597	0.01590519	0.01087739
12 N	-0.524158	-0.538027	-0.532935	0.013869	-0.005092	0.00811198	-0.00297831
13 N	-0.614082	-0.637611	-0.627867	0.023529	-0.009744	0.01376211	-0.00569927
14 C	-0.228288	-0.221384	-0.214265	-0.006904	-0.007119	-0.00403815	-0.0041639
15 C	-0.180297	-0.196146	-0.203341	0.015849	0.007195	0.00927008	0.00420836
16 C	0.176175	0.156275	0.151231	0.0199	0.005044	0.01163951	0.00295024
17 C	-0.227481	-0.247291	-0.239857	0.01981	-0.007434	0.01158687	-0.00434815
18 C	-0.194706	-0.244681	-0.271769	0.049975	0.027088	0.02923038	0.01584377
19 C	0.40269	0.37435	0.359786	0.02834	0.014564	0.01657607	0.00851848
20 C	-0.174381	-0.213942	-0.233757	0.039561	0.019815	0.02313923	0.01158979
21 H	0.189928	0.130947	0.113066	0.058981	0.017881	0.03449799	0.0104586
22 H	0.266686	0.250751	0.223928	0.015935	0.026823	0.00932038	0.01568877
23 H	0.212816	0.14305	0.108078	0.069766	0.034972	0.04080613	0.02045512
24 H	0.211028	0.144358	0.11028	0.06667	0.034078	0.03899528	0.01993222
25 F	-0.251833	-0.289926	-0.308477	0.038093	0.018551	0.0222806	0.01085048
26 C	0.002091	0.00243	0.01911	-0.000339	-0.01668	-0.00019828	-0.00975613
27 C	-0.314425	-0.315082	-0.306745	0.000657	-0.008337	0.00038428	-0.00487631
28 C	-0.23565	-0.213546	-0.205241	-0.022104	-0.008305	-0.01292863	-0.00485759
29 C	-0.191585	-0.171212	-0.16568	-0.020373	-0.005532	-0.01191617	-0.00323567
30 C	-0.271457	-0.270235	-0.263978	-0.001222	-0.006257	-0.00071475	-0.00365972
31 H	0.178269	0.168491	0.172929	0.009778	-0.004438	0.00571915	-0.00259579
32 H	0.215181	0.204664	0.186611	0.010517	0.018053	0.00615139	0.0105592
33 H	0.170177	0.17326	0.163038	-0.003083	0.010222	-0.00180325	0.00597885
34 H	0.174086	0.160194	0.137743	0.013892	0.022451	0.00812543	0.01313159
35 N	-0.458665	-0.47903	-0.483152	0.020365	0.004122	0.01191149	0.00241096
36 N	-0.403567	-0.426326	-0.418325	0.022759	-0.008001	0.01331174	-0.00467978
37 C	-0.369143	-0.363415	-0.345893	-0.005728	-0.017522	-0.00335031	-0.01024862
38 H	0.197313	0.182455	0.165265	0.014858	0.01719	0.00869044	0.01005443
39 H	0.148714	0.147751	0.138243	0.000963	0.009508	0.00056326	0.00556123
40 H	0.188274	0.183109	0.151267	0.005165	0.031842	0.00302101	0.01862439
41 C	-0.165936	-0.171159	-0.204531	0.005223	0.033372	0.00305493	0.01951928
42 C	0.538709	0.538181	0.508462	0.000528	0.029719	0.00030883	0.01738264
43 C	0.669038	0.656612	0.608256	0.012426	0.048356	0.00726797	0.02828342
44 C	0.027897	0.031229	-0.018116	-0.003332	0.049345	-0.00194889	0.02886189
45 H	0.179286	0.166348	0.132537	0.012938	0.033811	0.00756744	0.01977605
46 H	0.357991	0.353342	0.317742	0.004649	0.0356	0.0027192	0.02082244
47 H	0.175572	0.169903	0.127653	0.005669	0.04225	0.0033158	0.02471203
48 N	-0.473439	-0.489526	-0.489721	0.016087	0.000195	0.00940929	0.00011406
49 N	-0.520035	-0.594785	-0.572566	**0.07475**	-0.022219	**0.04372128**	-0.01299589

50 O	-0.482602	-0.52784	-0.569243	0.045238	0.041403	0.02645971	0.02421661
51 H	0.166113	0.154024	0.147072	0.012089	0.006952	0.00707086	0.00406622
52 H	0.18915	0.178026	0.184884	0.011124	-0.006858	0.00650643	-0.00401124
53 H	0.166773	0.163177	0.136224	0.003596	0.026953	0.0021033	0.01576481
54 H	0.177923	0.159686	0.141659	0.018237	0.018027	0.01066682	0.01054399
55 H	0.204151	0.187638	0.173819	0.016513	0.013819	0.00965845	0.00808273
56 H	0.20615	0.173819	0.163154	0.032331	0.010665	0.0189104	0.00623796
57 H	0.185001	0.155436	0.149111	0.029565	0.006325	0.01729257	0.00369949

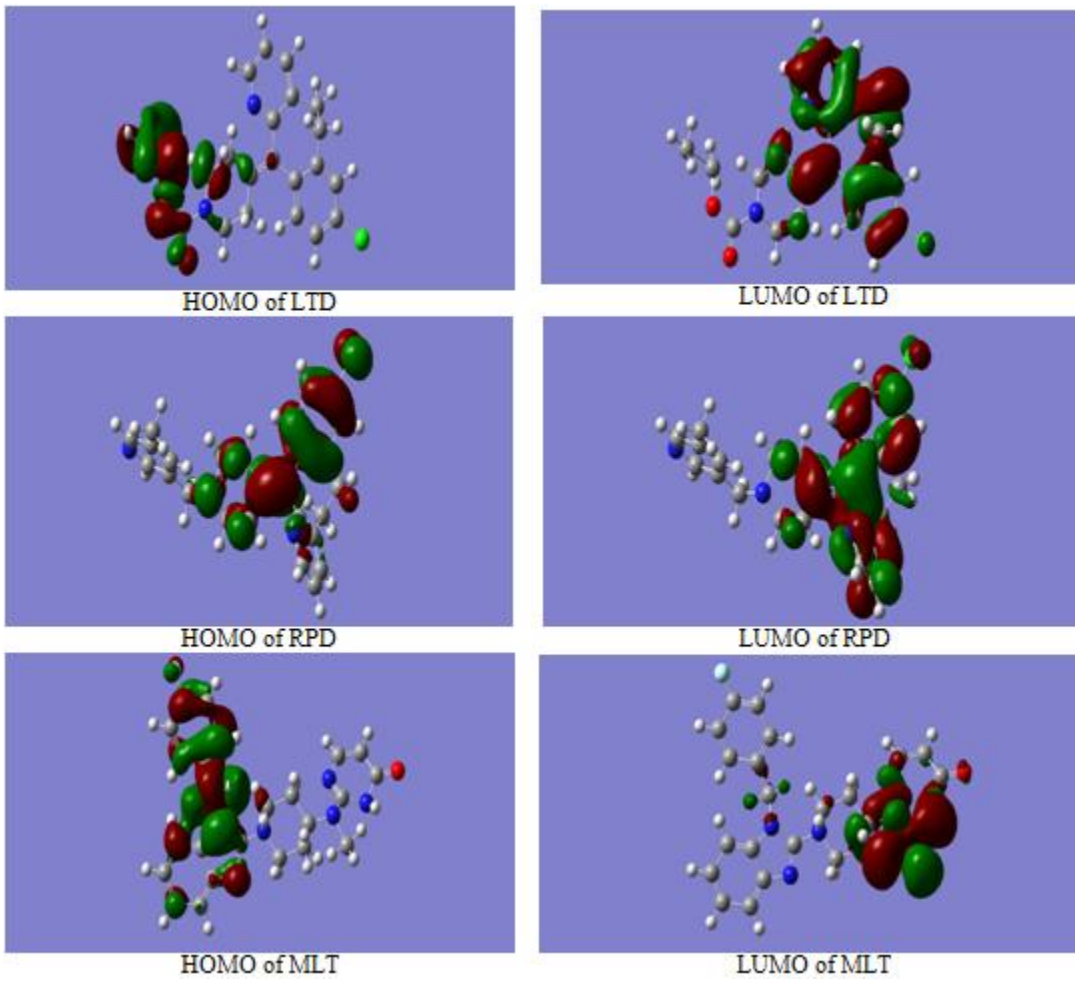

Figure 3 HOMO and LUMO diagrams of LTD, RPD and MLT using B3LYP/6-31G(d)

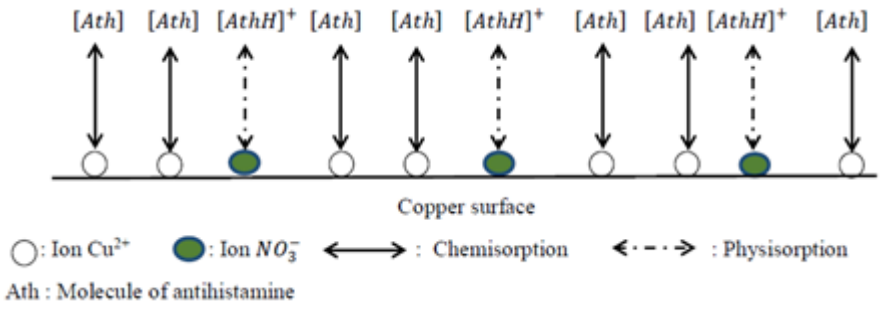

Figure 4 Schematic mechanism of copper corrosion inhibition by antihistamine

Conclusion

Global reactivity parameters calculated using density functional theory at B3LYP/6-31G(d) level shown that LTD, RPD and MLT are good inhibitors of copper corrosion in nitric acid solution. These molecules owe their good inhibition performance to the transfer of electrons from these molecule to the metal. Some quantum chemical parameters have shown that MLT has the best inhibition efficiency. The values of the electron transferred $(\Delta N)$and the electrophilicity index(ω) indicate that there is an exchange of electrons between each molecule and the metal, which helped to explain the mechanism of copper corrosion inhibition in nitric acid solution. Local reactivity parameters allow determining the probable electrophilic and nucleophilic attacks sites.

References

[1] O. K. Abiola and A. O. James. The effects of Aloe vera extract on corrosion and kinetics of corrosion process of zinc in HCl solution. Corrosion science, 2010, 52, 661-664.

[2] M. H. Hussin and M. J. Kassim. Electrochemical, thermodynamic and adsorption studies of catechin hydrate as natural mild steel corrosion inhibitor in 1 M HCl. International Journal of Electrochemical Science, 2011, 5, 1396–1414.

[3] Lukman O., Olasunkanmi, Lukman O. and Eno E. Ebenso. Experimental and computational studies on propanone derivatives of quinoxalin-6-yl-4, 5-dihydropyrazole as inhibitors of mild steel corrosion in hydrochloric acid. Journal of Colloid and Interface Science, 2020, 561,104-116.

[4] N. O. Eddy, S. A. Odoemelam and P. Ekwumemgbo. Inhibition of the corrosion of mild steel in H2SO4 by penicillin. Scientific Research and Essays, 2009, 4, 33-38.

[5] N. O. Eddy and S. A. Odoemelam, Inhibition of the corrosion of mild steel in acidic medium by penicillin V potassium. Advances in Natural and Applied Sciences, 2008, 2, 225–232.

[6] S. Ouattara, M. A. Tigori, V. Kouakou, P. M. Niamien and A. Trokourey. Combining DFT and QSPR methods for interpreting cefepime inhibiting properties in copper corrosion in 1M HNO3. Journal of Chemical, Biological and Physical Sciences, 2019, 9,253-273.

[7] I. B. Obot. Synergistic effect of nizoral and iodide ions on the corrosion inhibition of mild steel in sulphuric acid solution. Portugaliae Electrochimica Acta, 2009, 27, 539–553.

[8] I. B. Obot, N.O. and Obi-Egbedi. Adsorption properties and inhibition of mild steel corrosion in sulphuric acid solution by ketoconazole : experimental and theoretical investigation. Corrosion science, 2010, 52, 198–204.

[9] Bashir, S., Sharma, V., Kumar, S., Ghelichkhah, Z., Obotd, I. B. and Kumara, A. Inhibition Performances of Nicotinamide against Aluminum Corrosion in an Acidic Medium. Portugaliae Electrochimica Acta, 2020, 38, 107-123.

[10] Regina Fuchs-Godec and Gregor Zerjav. Corrosion resistance of high-level-hydrophobic layers in combinationwith Vitamin E as green inhibitor. Corrosion Science, 2015, 97, 7–16.

[11] A.S. Ekop and N. O. Eddy. Inhibitive and adsorptive properties of orphenadrine for the corrosion of mild steel in H2SO4. Australian Journal of Basic Applied Science, 2008, 2, 1258 -1263.

[12] E. E. Ebenso and N. O. Eddy, A. O. Odiongenyi. Corrosion inhibition and adsorption properties of methocarbamol on mild steel in acidic medium. Portugaliae Electrochimica Acta, 2009, 27:13–22.

[13] G. P. Cicileo, B. M. Rosales, F. E. Varela and J. R. Vilche. Comparative study of organic inhibitors of copper corrosion. Corrosion Science, 1999, 49, 1359-1375.

[14] G. Geceand and S. Bilgic. Quantum chemical study of some cyclic nitrogen compounds as corrosion inhibitors of steel in NaCl media. Corrosion Science, 2009, 8, 1876–1878.

[15] N. O. Obi-Egbedi, I. B. Obot, and M. I. El-Khaiary. Quantum chemical investigation and statistical analysis of the relationship between corrosion inhibition efficiency and molecular structure of xanthene and its derivatives on mild steel in sulphuric acid. Journal of Molecular Structure, 2011, 3, 86– 96.

[16] T. Gowrani. Gravimetric and Quantum Chemical Analysis of Brass Corrosion Inhibition by Inhibitors in Aqueous Medium. Chemical Science Review and Letters, 2018, 2278-6783.

[17] Z. El Adnani, M. Mcharfi, M. Sfaira, M. Benzakour, A. T. Benjelloun M. Ebu and Touhami. DFT theoretical study of 7-R-3 methylquinoxalin-2(1H)-thiones as corrosion inhibition in hydrochloric acid. Corrosion Science, 2013, 68, 223-230.

[18] D. K. Yadav, M. A. Quraishi, and B. Maiti. Inhibition effect of some benzylidenes on mild steel in HCl : An experimental and theoretical correlation. Corrosion science, 2012, 65, 254-266.

[19] M. H. Cohen, Nalewajski RF, In Topics in Current Chemistry, Heidelberg, Germany, 1996, p143.

[20] C. Lee, W. Yang and R. G. Parr. Development of the Colle-Salvetti correlation-energy formula into a

functional of the electron density. Physical Review B, 1988, 37, 785-789.
[21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and A. D. J. Fox, Gaussian, Inc., Wallingford, 2009, 09.
[22] Koopmans and T. Über die.Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines. Atoms. Physica 1934, 1, 104–13.
[23] R. G. Parr and R. G. Pearson. Absolute hardness: companion parameter to absolute electronegativity. Journal of the American Chemical Society, 1983, 105, 7512-7516.
[24] R. G. Parr, L. Szentpaly and S. Liu. Electrophilicity index. Journal of the American Chemical society, 1999, 121, 1922-1924.
[25] R. G. Pearson. Absolute Electronegativity and Hardness. Application to Inorganic Chemistry, 1988, 4,734-740.
[26] Parr, R.G. and Yang, W. Density functional approach to the frontier-electron theory. Journal of the American Chemical Society, 1984, 106, 4049–4050.
[27] Lee C, Yang W and Parr RG. Local softness and chemical reactivity in the molecules CO, SCN−and H2CO. Journal of Molecular structure : Theochem, 1988, 163, 305-313.
[28] W. Yang and W. J. Mortier. The use of global and local molecular parameters for the analysis of the gas-phase basicity of amines. Journal of the American Chemical Society, 1986, 108, 5708-5711.
[29] W. Yang and R. G. Parr. Hardness, softness and the Fukui function in the electronic theory of metals and catalysis. Proceeding of the National Academy of Sciences U.S.A, 1985, 82, 6723-6726.
[30] M. J. S. Dewar and W. Thiel. Ground states of molecules, the mndo method approximations and parameters. Journal of Chemical Physics, 1977, 99, 4899-4907.
[31] M. K. Awad, M. R. Mustafa and M. M. Abo Elnga. Computational simulation of the molecular Structure of some triazoles as inhibitors for the corrosion of metal surface. Journal of Molecular Structure (Theochem), 2010, 959, 66-74.
[32] S. G. Zhang, W. Lei, M. Z. Xia and F. Y. Wang. QSAR study on N-containing corrosion inhibitors: Quantum chemical approach assisted by topological index. Journal of Molecular Structure (Theochem), 2005, 732, 173-182.
[33] M. Lebrini, M. Lagrenée, H. Vezin, M. Traisnel and F. Bentiss. Experimental and theoretical study for corrosion inhibition of mild steel in normal hydrochloric acid solution by some new macrocyclic polyether compounds. Corrosion Science, 2007, 49, 2254-2269.
[34] N. Khalil, Quantum chemical approach of corrosion inhibition. Electrochimica Acta, 2003, 48,2635-2640.
[35] K. F. Khaled. Molecular simulation, quantum chemical calculations and electrochemical studies inhibition of mild steel by triazoles. Electrochimica Acta, 2008, 53, 3484-3492.
[36] N. A. Wazzan and F.M. Mahgoub. DFT Calculations for Corrosion Inhibition of Ferrous Alloys by Pyrazolopyrimidine Derivatives. Open Journal of Physical Chemistry, 2014, 4, 6-14.
[37] Obi-Egbedi N. O. and Obot I. B. Inhibitive properties, thermodynamic and quantum. chemical studies of alloxazine on mild steel corrosion in H2SO4. Corrosion Science, 2011, 53, 263-275.
[38] Saranya J., Sounthari P, Paranswari K. and Chitra S. Adsorption and density functional theory on Corrosion of mild steel by a quinoxaline derivative. Der Pharma Chemica, 2015, 8, 187-196.
[39] Geerlings P and De Proft F. Chemical reactivity as described by quantum chemical methods. International Journal of Molecular Sciences, 2002, 3: 276-309.
[40] I. B. Obot, and Z. M. Gasem. Theoretical evaluation of corrosion inhibition performance of some pyrazine derivatives. Corrosion Science, 2014, 83, 359-366.
[41] Lukovits I, Kalman E and Zucchi F. Corrosion inhibitors-correlation between electronic structure and efficiency. Corrosion, 2001, 1, 3-8.
[42] R. G. Parr, L. Szentpaly and S. Liu. Electrophilicity index. Journal of the American Chemical Society, 1999, 121, 1922-1924.
[43] P. Udhayakala and T. V. Rajendiran. A theoretical evaluation on benzothiazole derivatives as corrosion inhibitors on mild Steel. Der Pharma Chemica, 2015, 7, 92-99.

[44] F. Mendez and J. L. Gazquez. Reactivity of enolate ions : the Local Hard and Soft Acids and Bases Principle Viewpoint. Journal of the American Chemical Society, 1994, 116, 9298-9301.

Publication History
Received 11.01.2020
Revised 27.01.2020
Accepted 03.02.2020
Online 29.02.2020