The study of corrosion processes and their inhibition by organic inhibitors is a very active field of research. The presence of nitrogen, oxygen, phosphorous and sulphur in the organic molecules has a major effect on the inhibition efficiency and consequently on the phenomenon of adsorption on some metals surface. A great number of heterocyclic compounds were found to be excellent inhibitors of copper and steel corrosion. The inhibition effect mainly depends on some physicochemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons. DFT Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity. Thus, it has become a common practice to carry out quantum chemical calculations in corrosion inhibition studies.

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DFT and Quantum Chemical Studies for Heterocyclic Compounds

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Chapter 3
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DFT and Quantum Chemical Studies for Heterocyclic Compounds Used as Corrosion Organic Inhibitors

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Preface

The study of corrosion processes and their inhibition by organic inhibitors is a very active field of research. The presence of nitrogen, oxygen, phosphorous and sulphur in the organic molecules has a major effect on the inhibition efficiency and consequently on the phenomenon of adsorption on some metals surface. A great number of heterocyclic compounds were found to be excellent inhibitors of copper and steel corrosion. The inhibition effect mainly depends on some physicochemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons. DFT Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity. Thus, it has become a common practice to carry out quantum chemical calculations in corrosion inhibition studies. Recently, DFT Theoretical prediction of the efficiency of corrosion inhibitors has become very popular in parallel with the progress in computational hardware and the development of efficient algorithms which assisted the routine development of molecular quantum mechanical calculations.

This work discusses the dependence of inhibition efficiency of different organic compounds based on heterocyclic molecules to the DFT theoretical chemical parameters. The aim is to extend these investigations in order to discuss the relationship between quantum chemical calculations and experimental inhibition efficiencies by determining the quantum chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN), and the total energy (TE). It is difficult to prepare a review covering in details various aspects of this correlation. We will, therefore, concentrate our discussion in this work on the different interesting papers published by our research group in several international journals:

- Arab.J.Chem
- Int. J. Electrochem. Sci
- Res. Chem. Intermed

List of abbreviations

DFT Density functional theory

μ Dipole moment

χ Electronegativity

η Global hardness

A Electron affinity

f_k^+ electrophilic Fukui functions

ΔE Energy gap (i.e. $E_{LUMO} - E_{HOMO}$)

E_{HOMO} Energy of the highest occupied molecular orbital

E_{LUMO} Energy of the lowest unoccupied molecular orbital

Nu nucleophilicity indices

f_k^- nucleophilic Fukui functions

f(r) Fukui function

I Ionization potential

σ Softness

ΔN The fraction of electrons transferred

ΔN_{max} The maximum electronic charge for compounds

N_k The local nucleophilicity indexes

TE Total energy of the molecul

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General introduction

Corrosion is the destructive attack of a material by reaction with its environment. The serious consequences of the corrosion process have become a problem of worldwide significance. In addition to our everyday encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expensive overdesign; it also jeopardizes safety and inhibits technological progress. The multidisciplinary aspect of corrosion problems combined with the distributed responsibilities associated with such problems only increase the complexity of the subject. Corrosion control is achieved by recognizing and understanding corrosion mechanisms, by using corrosion- resistant materials and designs, and by using protective systems, devices, and treatments. The use of inhibitors has been found to be one of the best options available for the protection of metals against corrosion. The study of corrosion processes and their inhibition by organic inhibitors is a very active field of research [1]. Many researchers report that the inhibition effect mainly depends on some physicochemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons, and so on [2,3]. The inhibiting mechanism is generally explained by the formation of a physically and/or chemically adsorbed film on the metal surface [4,5]. It is well known that organic compounds which act as inhibitors are rich in heteroatoms, such as sulphur, nitrogen, and oxygen [6,7]. These compounds and their derivatives are excellent corrosion inhibitors in a wide range of media and are selected essentially from empirical knowledge based on their macroscopic physico-chemical properties. Recently, theoretical prediction of the efficiency of corrosion inhibitors has become very popular in parallel with the progress in computational hardware and the development of efficient algorithms which assisted the routine development of molecular quantum mechanical calculations [8]. Due to the enormous complexity of this type of

studies which need to consider the metallic surface, inhibitor and solvent molecules, theoretical calculations of the corrosion inhibition processes cannot be achieved in a rigorous way from the viewpoint of quantum chemistry.

Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity [9]. Thus, it has become a common practice to carry out quantum chemical calculations in corrosion inhibition studies. The concept of assessing the efficiency of a corrosion inhibitor with the help of computational chemistry is to search for compounds with desired properties using chemical intuition and experience into a mathematically quantified and computerized form. Once a correlation between the structure and activity or property is found, any number of compounds, including those not yet synthesized, can be readily screened employing computational methodology [10] and a set of mathematical equations which are capable of representing accurately the chemical phenomenon under study [11,12]. Recently, density functional theory (DFT) is used to investigate the electronic structure, principally the ground state of many-body systems, in particular atoms, molecules and the condensed phases. The main objective of DFT is to replace the many-body electronic wave function with the electronic density as the basic quantity [13]. Any exchange functional can be combined with any correlation functional in DFT calculations.

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1 DFT and Quantum chemical investigation of molecular properties of substituted pyrrolidines

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1.1. Introduction

The chemistry of heterocyclic molecules containing functional group and heteroelement atoms is attracting current interest in life sciences due to their specificity for biological targets [1,2]. These compounds are also of importance for building polynuclear complexes [3] as models for bioorganic systems [4-8] as well as for the discovery of new catalyst precursors [9]. A number of these compounds were found to be excellent inhibitors of copper corrosion [10, 11]. The presence of nitrogen, oxygen, phosphorous and sulphur in these molecules has a major effect on the inhibition efficiency and consequently on the phenomenon of adsorption on some metals surface. In this article, we design five molecules based on heterocyclic functional pyridine and pyrimidine such as 1-{2-[(2-hydroxyethyl)thio]ethyl}pyrrolidin-2-one (**HTEP**) [12-14]; [2-(2-oxo-pyrrolidin-1-yl)-ethyl]-phosphonic acid diethyl ester (**EOEP**); 2-(2-oxopyrrolidin-1-yl)ethyl]thio}acetic acid (**OETA**) [12] (Bouklah et al., 2006); (2-pyridin-4-yl-ethyl]thio}acetic acid (**PTA**) [15, 16]; pyridine (**PY**) [17] (Figure 1). Theoretical calculations were carried out with Gaussien 94 [18]. A conformation analysis was performed, for the inhibitors, on all bonds using an option "scan'' in the

EMO program, and then founded structures were minimized using Molecular Force Field EMO (MM2-Allinger) and fully optimized at DFT level using Hybrid B3LYP functional density with 6-31G* basis set.

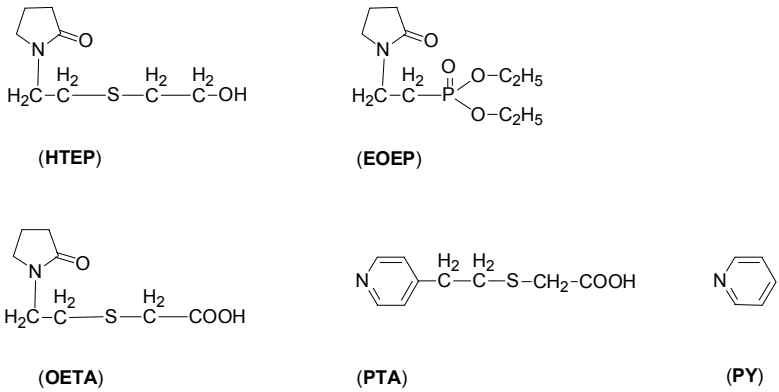

Fig.1: Molecular Structure of the inhibitors

1.2. Calculations methods

Quantum mechanical geometry optimizations, thermodynamic properties, dipole moments and frontier molecular orbital properties of all compounds were performed with the Gaussian 94 program package. They were carried out by using the 6-31G* basis set. Calorific capacities, heats of formation and entropies have been calculated at different temperature: 100K, 298.15K, 1000K, 1200K, 1500K and 2000K. In order to understand the phenomenon of corrosion, we examined the molecular HOMOs (presumably the π_{donor}) and molecular LUMOs (presumably the $\pi_{acceptor}$) generated via Gaussian 94 by using the HF/6-31G* method (Table 1).

Table 1

Calculated quantum chemical parameters of studied compounds.

	TE u.a	E(HOMO) u.a	E(LUMO) u.a	ΔE u.a	μ Debye	E %
EOEP	-1090,2006	-0,2428	0,0229	0,2657	3,7437	86
PTA	-952,9752	-0,2366	-0,0245	0,2122	4.4754	82
HTEP	-917,2736	-0,2239	0,0244	0,2483	5.2577	89
OETA	-991,3242	-0,2324	-0,0058	0,2266	4.1691	83
PY	-248.2850	-0.2526	-0.0225	0,2301	2.1921	17

The 1-{2-[(2-hydroxyethyl)thio]ethyl}pyrrolidin-2-one (**HTEP**) and {[2-(2-oxopyrrolidin-1-yl)ethyl]thio}acetic acid (OETA), were synthesized and tested as corrosion inhibitors for steel in 0.5 M H_2SO_4. The study was carried out by wt. loss measurements, potentiodynamic polarization, linear polarization resistance (Rp) and electrochemical impedance spectroscopy (EIS) methods. The inhibition efficiency increases with the concentration of (**HTEP**) to attain 89% at 5.10^{-3} M with good agreement between the various methods explored. Therefore, theoretical studies will a good set to explain these results.

1.3. Results and discussion

The corrosion inhibition of steel and copper or their alloys by different heterocyclic compounds, as pyrazol, triazole, imidazole and tetrazole derivatives depends essentially on the structure of the inhibitor itself which includes the number of adsorption active centre in the molecule, the nature of the metal and the aggressive solution [19]. To investigate the influence of electronic structure on the efficiency of synthesis bipyrazolic compounds: 1-{2-[(2-hydroxyethyl)thio]ethyl}pyrrolidin-2-one (**HTEP**); [2-(2-oxo-pyrrolidin-1-yl)-ethyl]-phosphonic acid diethyl ester (**EOEP**); 2-(2-oxopyrrolidin-1-yl)ethyl]thio}acetic acid (**OETA**); (2-pyridin-4-yl-ethyl]thio}acetic acid (**PTA**);

pyridine (**PY**), some parameters such as the energy of molecular orbital, E_{HOMO}, E_{LUMO} and the dipole moment (μ) were carried out. The results are given in table 1. The energy of HOMO is often associated with the electron donating ability of a molecule; high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy and empty molecular orbital. Therefore, the energy of LUMO indicates the ability of the molecule to accept electrons [20, 21]. The presence of five atoms of nitrogen in the molecules has a major effect on the inhibition efficiencies and consequently on the phenomenon of adsorption on the copper surface. These five atoms of nitrogen constitute an active adsorption centre in these inhibitors. Following the E_{HOMO} from table 1 looks apparently easier for the molecule to offer electrons to unoccupied d-orbitals of copper and in that case the higher inhibition efficiency is expected. The higher HOMO energy from **HTEP › OETA › EOEP** and **PTA › PY,** can be used as one of the parameters for the explanation of its good inhibitors performance. Consequently, the smaller energy gap is reflected in a stronger chemisorptions bond and perhaps greater inhibition efficiency [22]. Lower values of dipole moments (μ) will favour accumulation of the inhibitor in the surface layer and therefore higher inhibition efficiency [23]. Meanwhile, several authors state that the inhibition efficiency increases with increasing values of dipole moment [24, 25]. On the other hand, survey of literature reveals that several irregularities appeared in case of correlation of dipole moment with inhibitor of efficiency [26, 27]. The vibrational frequencies were also calculated with AM1 semi empirical and HF/6-31G (d) methods. The frequency values computed at these levels contain known systematic errors [28]. We therefore have used the scaling factor values of 0.9900 [29] and 0.8929 [30, 31] for AM1 and HF/6-31G (d) respectively. The assignment of the calculated wave numbers is aided by the animation option of Gauss View 94 graphical interface for Gaussian programs, with gives a visual presentation of the shape of the vibrational modes.

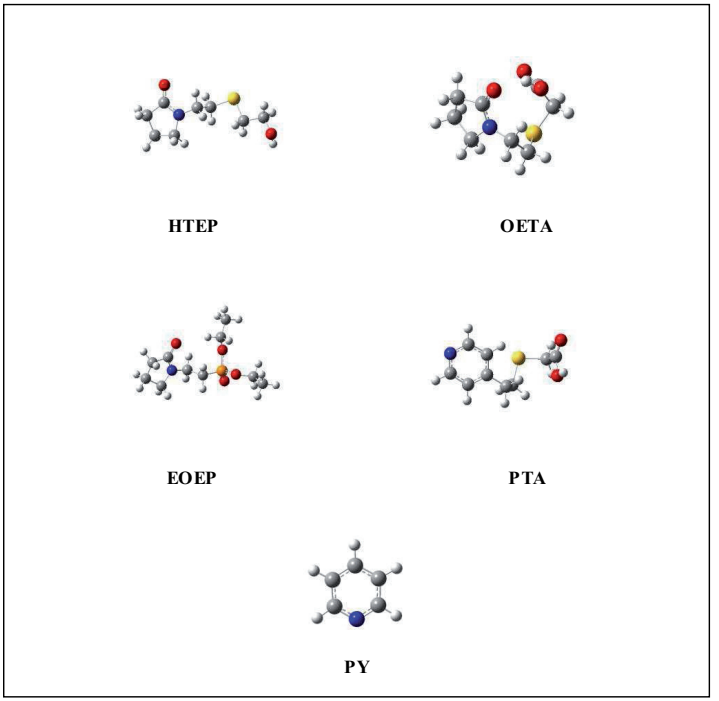

Fig.2. Optimized Structures of the studied inhibitors

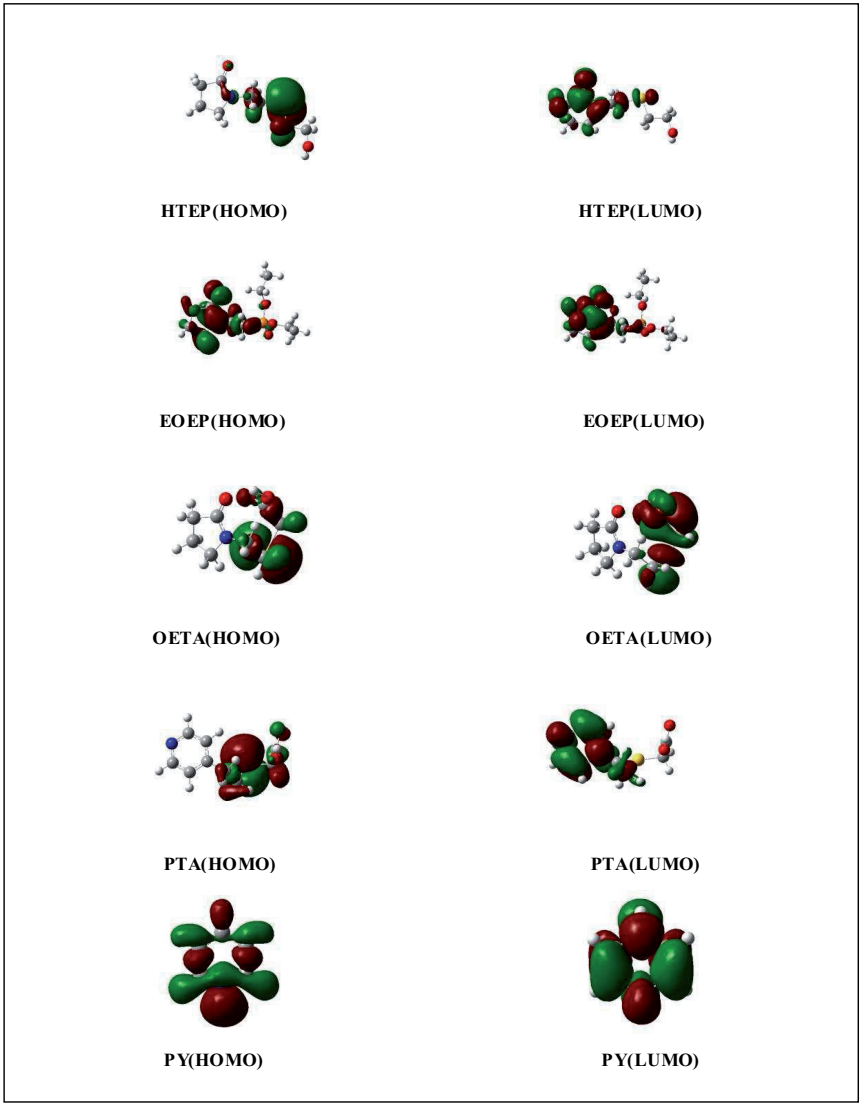

Fig. 3: Orbital form for all these compounds

1.4. Conclusion

It can be concluded on the basis of the result obtained that the:

- The selection of parameters is in important step in theoretical study. The relationship between the parameter (s) and activity should be strong, and therefore efficiency predictions will be more promising.
- The high values of the thermodynamic parameters suggest higher stability for molecules studied.
- The HOMO energy calculations show that bipy1 molecule has the higher energy therefore they could be better corrosion inhibitors of the series studied
- The calculated vibrational frequencies, reveal that the results of the calculation before applying the scale factor in AM1 method give largest deviations from the experimental data, whereas the frequencies obtained in HF/6-31G* method is in good agreement with the experimental wavenumbers without using the factor scaling.
- The estimation *a priori* of the parameters discussed by quantum-chemical methods is important for the molecular design of compounds with given properties and may serve as the basis for the acceptance of expert solutions on the expediency of a synthesis, laborious, prolonged, requiring complex apparatus, vigorous conditions, with expensive and toxic reagents.

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2 Theoretical study using DFT calculations on inhibitory action of four pyridazines on corrosion of copper in nitric acid

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2. 1. Introduction

Density functional theory (DFT) has become very popular in recent years. This is justified based on the pragmatic observation that it is less computationally intensive than other methods with similar accuracy. This theory has been developed more recently than other ab initio methods. Because of this, there are classes of problems not yet explored with this theory, making it all the more crucial to test the accuracy of the method before applying it to unknown systems [1]. The most fundamental difference between DFT and MO theory must never be forgotten: DFT optimizes an electron density while MO theory optimizes a wave function. So, to determine a particular molecular property using DFT, we need to know how that property depends on the density, while to determine the same property using a wave function, we need to know the correct quantum mechanical operator [2].

The concept of assessing the efficiency of an inhibitor of corrosion with the help of computational chemistry is to search for compounds with desired properties using chemical intuition and

experience into a mathematically quantified and computerized form. Once a correlation between the structure and activity or property is found, any number of compounds, including those not yet synthesized, can be readily screened employing computational methodology and a set of mathematical equations which are capable of representing accurately the chemical phenomenon under study [3-5].

The most efficient inhibitors are the organic compounds that have π bonds, heteroatoms (P, S, N, and O). The inhibition effect mainly depends on some physicochemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons, and soon [6,7]. The inhibiting mechanism is generally explained by the formation of a physically and/or chemically adsorbed film on the metal surface [8, 9]. The encouraging results obtained by pyridazine compounds in many papers incited us to develop some theoritical calculations to correlate efficiency to the molecular structure of inhibitors used [10-15]. Recently, theoretical explanations of the efficiency of corrosion inhibitors become very possible in parallel with the progress in computational hardware and the development of efficient algorithms [16-18].

In the present paper, four pyridazines (P1, P2, P3 and P4) derivatives were newly synthesized and tested as corrosion inhibitors of the copper in 2M HNO_3. The chemical structures of the studied pyridazine derivatives are given in Figure 1.

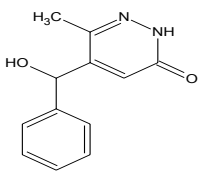	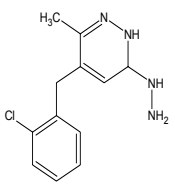	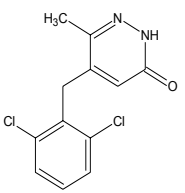	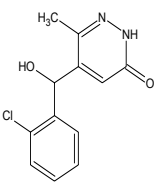
5-[hydroxy(phenyl) methyl]-6-methylpyri dazin-3(2*H*)-one (P1)	4-(2-chlorobenzyl)-6-hydrazino-3-methyl-1,6-dihydropyridazine (P2)	5-(2,6-dichlorobenzyl)-6-methylpyridazin-3(2*H*)-one (P3)	5-[(2-chlorophenyl) (hydroxy)methyl]-6-methyl pyridazin-3(2*H*)-one (P4)

Fig. 1. The proposed structure of the studied pyridazine derivatives.

Recently, density functional theory has been used to analyze the electronic and geometric characteristics of the inhibitor/surface mechanism and to describe the structural nature of the inhibitor on the process of corrosion [19]. Furthermore, it is considered a very useful technique to analyze the experimental data [20]. The electronic properties of inhibitors such as the highest occupied molecule orbital (HOMO), the lowest unoccupied molecule orbital (LUMO), Gap energy difference between E_{HOMO} and E_{LUMO} and dipole moments have been achieved the appropriate correlation

2.2. Computational details

DFT (density functional theory) methods were used in this study. These methods have become very popular in recent years because they can reach exactitude similar to other methods (ab initio, QSAR : Quantitative Structure-Activity Relationships,…) in less time and less expensive from the computational point of view. In agreement with the DFT results, energy of the fundamental state of a polyelectronic system can be expressed through the total electronic density, and in fact, the use of electronic density instead of wave function for calculating the energy constitutes the fundamental base of DFT [21]. All calculations were done by GAUSSIAN 03 W software [22], using the B3LYP functional [23, 24] and a 6-31G* basis set [24]. The B3LYP, a version of DFT method, uses Becke's three-parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang, and Parr (LYP) [23, 24]. The geometry of all species under investigation was determined by optimizing all geometrical variables without any symmetry constraints. Frontier molecular orbitals (*HOMO* and *LUMO*) may be used to predict the adsorption centers of the inhibitor molecule. For the simplest transfer of electrons, adsorption should occur at the part of the molecule where the softness, σ , which is a local property, has the highest value. According to Koopman's theorem [25], the energies of the *HOMO* and the *LUMO* orbitals of the inhibitor molecule are related to the ionization

potential, I, and the electron affinity, A, respectively, by the following relations: $I = -E_{HOMO}$ and $A = -E_{LUMO}$. Absolute electronegativity, χ, and absolute hardness, η, of the inhibitor molecule are given by [26]. $\chi = \frac{I + A}{2}$ and $\eta = \frac{I - A}{2}$. The softness is the inverse of the hardness: $\sigma = \frac{1}{\eta}$. The obtained values of χ and η are used to calculate the fraction of electron transferred, ΔN, from the inhibitor to metallic surface as follow [27]: $\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2\ \eta_{Cu} + \eta_{inh}}$. Using a theoretical value, $\chi_{Cu} = 4.48 eV/mol$ and value of $\eta_{Cu} = 0 eV/mol$ for copper according to Pearson's electronegativity scale assuming that for a metallic bulk $I = A$, because they are softer than neutral metallic atoms [26].

2.3. Results and discussion

Table 1 summarized the inhibition efficiency (E_w%) obtained by addition of P1, P2, P3 and P4 at different concentrations on the corrosion of copper in 2M HNO_3 solution determined by weight loss at 1 h.

Table 1 indicates clearly a decrease in the corrosion rate in the presence of P1, P2, P3 and P4. This effect is hugely marked at higher concentration of inhibitors. The inhibitive action is more explicit by E_w% data which increases with inhibitor concentration to reach 93.2% for P1, 83.6% for P2, 96.2% for P3 and 94.3% for P4 at 10^{-3}M. Then all inhibitors studied inhibit the corrosion of copper in 2M HNO_3, but the inhibitor P3 is found to exhibit the best inhibitory action.

Table 1

Gravimetric results of copper in 2M HNO_3 without and with addition of inhibitors at 303 K [14].

Conc(M)	P1	P2	P3	P4
	E_w (%)	E_w (%)	E_w (%)	E_w(%)
Blank	-	-	-	-
1×10^{-3}	**93.2**	**83.6**	**96.2**	**94.3**
5×10^{-4}	92.8	83.4	92.6	82.5
1×10^{-4}	88.1	71.2	90.1	59.4
5×10^{-5}	75.8	51.5	65.3	39.7

1×10^{-5}	63.0	40.2	28.6	12.6
1×10^{-6}	31.9	22.6	13.8	02.0

The corrosion inhibition was attributed to the adsorption of the molecule species P1, P2, P3 and P4. It was shown from experimental results that the investigated compounds were good inhibitors, but no giving further insight into the correlations between this inhibition and the electronic properties such as the highest occupied molecule orbital (HOMO), the lowest unoccupied molecule orbital (LUMO), Gap energy difference between E_{HOMO} and E_{LUMO} and dipole moments. Thus the density functional theory was applied to study correlation with experimental results. The optimized geometry structures of the studied compounds are illustrated in Figure 2. The optimization process (the global minimum energy information of the materials is achieved) was fully done using B3LYP/ 6-31G* calculation.

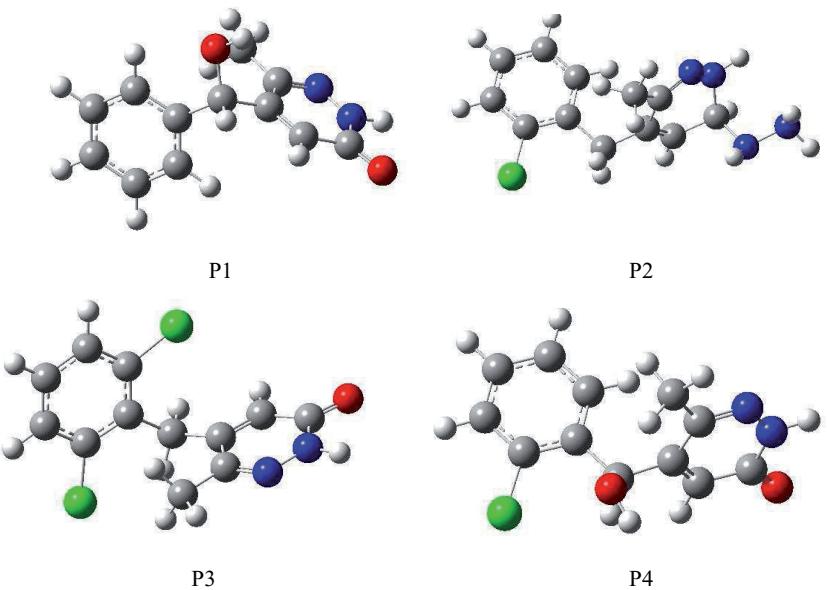

Fig. 2. Optimized structure of studied molecules obtained by B3LYP/6-31G* level.

In table 2, we present The calculated quantum chemical parameters of the of the studied pyridazines.

Table 2

Calculated quantum chemical parameters of the pyridazine derivatives.

Quantum parameters	P1	P2	P3	P4
E_{HOMO} (eV)	-6.357	-5.425	-6.173	-6.371
E_{LUMO} (eV)	-1.681	-0.757	-1.538	-1.767
ΔE gap (eV)	4.676	4.668	4.634	4.604
E_w %	93.25	83.63	96.16	94.32
μ (debye)	2.8125	1.5722	4.8566	2.1127
I (eV)	6.357	5.425	6.173	6.371
A (eV)	1.681	0.757	1.538	1.767
χ (eV)	4.019	3.091	3.855	4.069
η (eV)	2.338	2.334	2.317	2.302
ΔN	0.09859	0.29756	0.13487	0.08927
σ	0.428	0.428	0.431	0.434
TE (kcal /mol)	-724.425	-1139.563	-1560.655	-1177.935

It is known that the value of E_{HOMO} is often associated with the electron donating ability of inhibitor molecule, higher values of E_{HOMO} is an indication of the greater ease of donating electrons to the unoccupied d orbital of metal. The value of E_{LUMO} is related to the ability of the molecule to accept electrons, lower values of E_{LUMO} shows the inhibitor molecule would accept electrons. Consequently, the value of ΔE_{gap} provides a measure for the stability of the formed complex on the metal surface. The lower value of ΔE has, the higher stability is for the formed complex. The value of ΔE for P1, P2, P3 and P4 are 4.676, 4.668, 4.634 and 4.604 eV, respectively. The decrease of the energy difference between the frontier molecule orbital means that the quality of the formed films by P3 and P4 are superior to P1 and P2. From these theoretical calculations carried out for studied molecules P1, P2, P3 and P4, it can be concluded that the electronic properties of the inhibitors are correlated with their inhibition performance. When the HOMO orbital for P1, P2, P3 and P4 (Figure 3) is analyzed, it is found that the highest occupied molecule orbital (HOMO) is only in the atoms of pyridazine cycle for P1 and P2, this being the preferred zone for nucleophilic attack. For P3 and P4, the HOMO is localized in the atoms of pyridazine cycle and in Cl atom (P3) and in O (OH (for

P4) consequently this is the favourite sites for interaction with the metal surface. Furthermore, the P3 and P4 molecules present structures in which the most reactive sites can effectively interact with the metal surface. This could explain their stronger interactions with the metal surface and having a better inhibition effect for copper than P2.

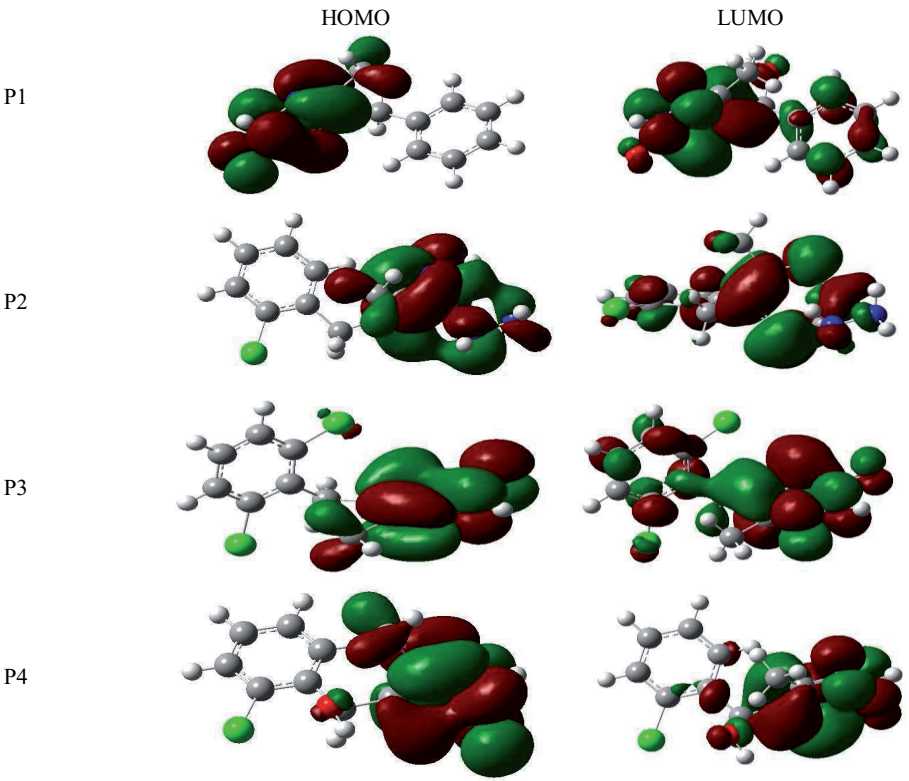

Fig. 3. Schematic representation of HOMO and LUMO molecular orbital of studied molecules.

The total energy of the best inhibitor P3 is equal to -1560.652 eV. This result indicated that P3 is favourably adsorbed through the active centers of adsorption and especially the presence of two chloride atoms on 2 and 6 positions on phenyl ring.

Figure 4 shows the correlation diagram of frontier molecular orbitals for the investigated inhibitors and their calculated ΔE. The HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the innermost (lowest energy) orbital that has room to accept electrons. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants [3]. The energy of the HOMO is directly related to the ionization potential and the energy of the LUMO is directly related to the electron affinity. A large HOMO–LUMO gap implies high stability for the molecule in chemical reactions [28]. Gece stated that the less negative HOMO and the smaller energy gap reflected stronger chemisorbed bond and greater inhibitor efficiency. In this work, we have shown that pyridazine P3 acted as physical adsorption [14], then P1, P2 and P4 which exhibited higher efficiency have both less negative HOMO and smaller ΔE values compared to that of P2.

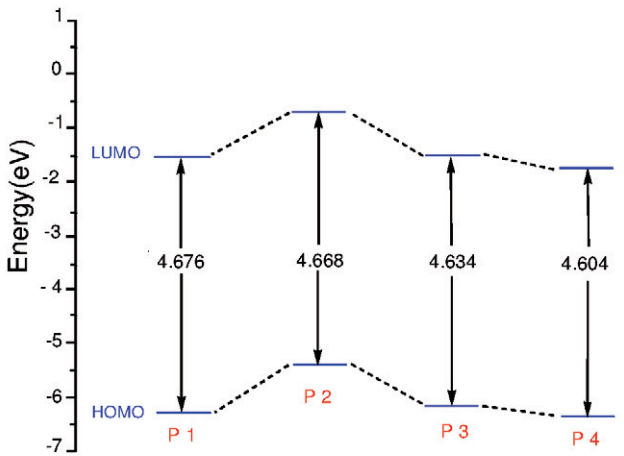

Fig. 4. Correlation diagram of frontier molecular orbitals for the investigated inhibitors and their calculated ΔE (eV).

2.4. Conclusion

In theoretical works, it is important to show that the results obtained from the calculations agree well with experimental values. In this study, the calculated quantum chemical parameters of four pyridazine derivatives are compared with their experimental inhibition efficiencies. The following conclusions can be deduced from the present study:

- Using the DFT/B3LYP method, the inhibition efficiency of four substituted pyridazine compounds may be correlated to their molecular structure.
- P1, P2 and P4 which exhibited higher efficiency have both less negative HOMO and smaller ΔE values compared to that of P2.
- The total energy of the best inhibitor P3 is the lowest among the compounds studied. This result indicated that P3 is favourably adsorbed through the active centers of adsorption on Copper surface,

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3 Quantum Chemical Study of Some Triazoles Compounds as Corrosion Inhibitors of Copper in Acid Media

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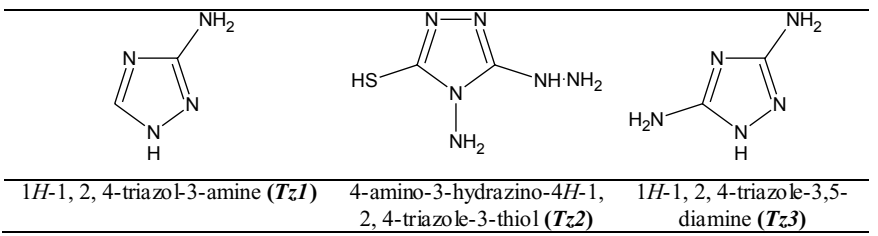
3.1. Introduction

Study of corrosion inhibition is a very active field of research. Several classes of organic compounds are widely used as corrosion inhibitors for metals in acid environments [1–16]. Experimental means are useful to explain the inhibition mechanism but they are often expensive and time-consuming. Ongoing hardware and software advances have opened the door for powerful use of theoretical chemistry in corrosion inhibition research. Several quantum chemical methods and molecular modeling techniques have been performed to correlate the inhibition efficiency of the inhibitors with their molecular properties [17–23]. Using theoretical parameters helps to characterize the molecular structure of the inhibitors and to propose their interacting mechanism with surfaces [24]. Some studies have shown that the inhibition of the corrosion process is mainly described by the formation of donor–acceptor surface complexes between free or π-electrons of an organic inhibitor, mostly containing nitrogen, sulphur or oxygen atoms, and a vacant d-orbital of a metal [25–34]. Among the various nitrogenous compounds studied as inhibitors, triazoles have been

considered as environmentally acceptable chemicals. Many substituted triazoles compounds have been recently studied in considerable details as effective corrosion inhibitors for steel and copper in acidic media [35–48].

The inhibitive properties of three different organic compounds, namely 1*H*-1, 2, 4-triazol-3-amine (*Tz1*), 4-amino-3-hydrazino-4*H*-1, 2, 4-triazole-3-thiol (*Tz2*) and 1*H*-1, 2, 4-triazole-3,5-diamine (*Tz3*) have been reported in a previous experimental study [49, 50]. The aim of this paper is to extend these investigations in order to discuss the relationship between quantum chemical calculations and experimental inhibition efficiencies of the inhibitors by determining the quantum chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN), and the total energy (TE). The chemical structures of the compounds studied are given in Fig. 1.



1*H*-1, 2, 4-triazol-3-amine **(*Tz1*)**	4-amino-3-hydrazino-4*H*-1, 2, 4-triazole-3-thiol **(*Tz2*)**	1*H*-1, 2, 4-triazole-3,5-diamine **(*Tz3*)**

Fig. 1 The molecular structures of the investigated inhibitors.

3.2. Calculation method

DFT (density functional theory) methods were used in this study. These methods have become very popular in recent years because they can reach exactitude similar to other methods (ab initio, *QSAR*: Quantitative Structure-Activity Relationships,…) in less time and less expensive from the computational point of view. In agreement with the *DFT* results, energy of the fundamental state of

a polyelectronic system can be expressed through the total electronic density, and in fact, the use of electronic density instead of wave function for calculating the energy constitutes the fundamental base of *DFT* [51]. All calculations were done by GAUSSIAN 03 W software [52], using the *B3LYP* functional [53, 54] and a *6-31G** basis set [54]. The *B3LYP*, a version of *DFT* method, uses Becke's three-parameter functional (B3) and includes a mixture of HF with *DFT* exchange terms associated with the gradient corrected correlation functional of Lee, Yang, and Parr (*LYP*) [53, 54]. The geometry of all species under investigation was determined by optimizing all geometrical variables withoutany symmetry constraints. Frontier molecular orbitals (*HOMO* and *LUMO*) may be used to predict the adsorption centers of the inhibitor molecule. For the simplest transfer of electrons, adsorption should occur at the part of the molecule where the softness, σ , which is a local property, has the highest value. According to Koopman's theorem [55], the energies of the *HOMO* and the *LUMO* orbitals of the inhibitor molecule are related to the ionization potential, *I*, and the electron affinity, *A*, respectively, by the following relations: $I = -E_{HOMO}$ and $A = -E_{LUMO}$. Absolute electronegativity, χ , and absolute hardness, η , of the inhibitor molecule are given by [56]. $\chi = \frac{I + A}{2}$ and $\eta = \frac{I - A}{2}$. The softness is the inverse of the hardness: $\sigma = \frac{1}{\eta}$. The obtained values of χ and η were used to calculate the fraction of electrons transferred ΔN, from the inhibitor to metallic surface [54, 56–59] as follows:

$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2\ (\eta_{Cu} + \eta_{inh})}$. In order to calculate the fraction of electrons transferred, a theoretical value for the electronegativity of bulk copper was used $\chi_{Cu} = 4.48\ eV\ mol^{-1}$ [60], and a global hardness of , $\eta_{Cu} = 0\ eV\ mol^{-1}$ by assuming that for a metallic bulk $I = A$ [59] because they are softer than the neutral metallic atoms.

3.3. Results and discussion

The corrosion rate (W_{corr}) of copper in 2M HNO_3 solution at various contents of triazole derivatives, tested was determined after 1 h of immersion period at 303 ± 1 K. In the case of the weight loss method, the inhibition efficiency (E_w %) was determined by the following relation:

$$E_w\% = \left(1 - \frac{W_{corr}}{W^{\circ}_{corr}}\right) \times 100$$

Where W^{o}_{corr} and W_{corr} are the corrosion rates of pure copper samples in the absence and presence of the organic compounds, respectively.

The inhibition of copper using substituted triazoles as corrosion inhibitors were investigated experimentally. Table 1 summarized the inhibition efficiency (E_w%) obtained by addition of Tz1, Tz2 and Tz3 at different concentrations on the corrosion of copper in 2 M HNO_3 solution determined by weight loss at 1 h.

Table 1 clearly indicates a decrease in the corrosion rate in the presence of Tz1, Tz2 and Tz3. This effect is hugely marked at higher concentrations of inhibitors. The inhibitive action is more explicit by E_w% data which increase with inhibitor concentration to reach 82.2 % for Tz1, 91.7 % for Tz2 and 86.5 % for Tz3 at 10^{-2} M. Then, all inhibitors studied inhibit the corrosion of copper in 2 M HNO_3, but the inhibitor Tz2 is found to exhibit the best inhibitory action. The classification of these inhibitors according to its inhibition efficiency is:

Tz2 > Tz3 > Tz1.

Table 1

summarized the inhibition efficiency (*E*%) obtained by addition of *Tz1*, *Tz2* and *Tz3* at different concentrations on the corrosion of copper in 2 M HNO_3 solution determined by weight loss at 1 h.

Conc (M)	*Tz1*	*Tz2*	*Tz3*
	E_w (%)	E_w (%)	E_w (%)
Blank	-	-	-
1×10^{-2}	**82.19**	**91.74**	**86.46**
5×10^{-3}	77.86	87.92	81.29
1×10^{-3}	55.95	74.49	69.72
5×10^{-4}	47.86	58.37	53.65
1×10^{-4}	19.49	50.28	52.47
5×10^{-5}	15.67	37.08	37.08
1×10^{-5}	05.62	33.37	33.31

Theoretical chemistry has been used recently to explain the mechanism of corrosion inhibition, such as quantum chemical calculations, which have been proved to be a very powerful tool for studying the mechanism [61–67]. The reactive ability of the inhibitor is closely linked to their frontier molecular orbitals (*MO*), including highest occupied molecular orbital, *HOMO*, and

lowest unoccupied molecular orbital, *LUMO*, and the other parameters such as hardness, dipole moment (μ), total energy (*TE*) and softness. Quantum chemical studies have been successfully performed to link the corrosion inhibition efficiency with molecular orbitals (*MO*) energy levels for some kinds of organic compounds, e.g., amides [68, 69], amino acids and hydroxy carboxylic acids [70], pyridine-pyrazole compound [71], sulfonamides [72], triazoles compounds [73] to mention but a few. Accordingly, quantum chemical calculations are performed to investigate the structural parameters affect the inhibition efficiency of inhibitors. The optimized molecular structures of the studied molecules using hybrid *DFT* functional (*B3LYP/6-31G* (d)*) are shown in Fig. 2.

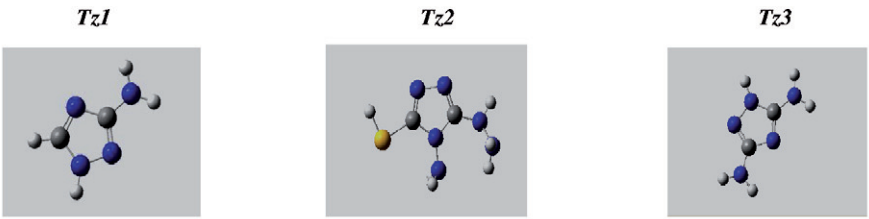


Fig. 2. Optimized structure of studied molecules obtained by B3LYP/6-31G* level.

Quantum chemical parameters obtained from the calculations which are responsible for the inhibition efficiency of inhibitors such as the energies of frontier molecular orbitals (E_{HOMO}) and (E_{LUMO}), the separation energy (E_{LUMO} - E_{HOMO}), ΔE, dipole moment(μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the total energy (*TE*) and the fraction of electrons transferred from the inhibitor to copper surface (ΔN), are given in Table 2.

Table 2

Calculated quantum chemical parameters of the studied compounds.

Quantum parameters	*Tz1*	*Tz2*	*Tz3*
E_{HOMO} (eV)	-6.100144	-6.299792	-5.528944
E_{LUMO} (eV)	-0.3468	-1.050464	-0.685984
ΔE gap (eV)	5.7528	5.249328	4.84296
E_w %	82.2%	91.7%	86.5%
μ (debye)	1.3817	5.2811	2.9140
$I = -E_{HOMO}$ (eV)	6.100144	6.299792	5.528944

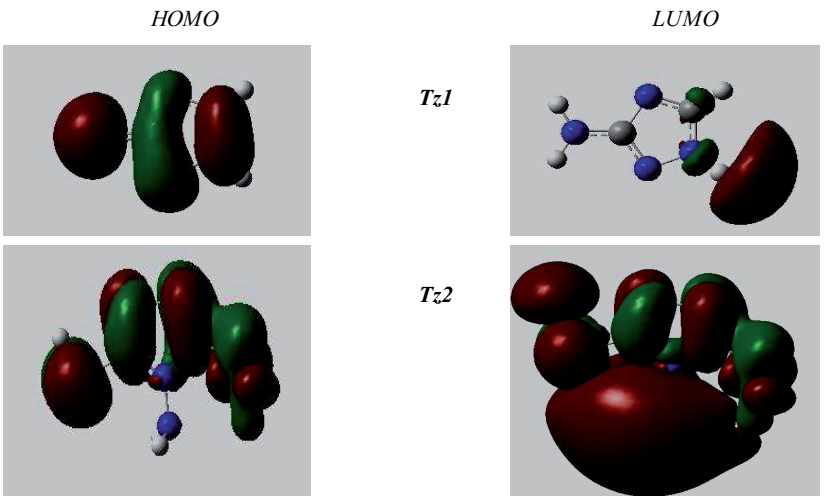
$A = -E_{LUMO}$ (eV)	0.3468	1.050464	0.685984
$\chi = \frac{I + A}{2}$ (eV)	3.22347	3.67513	3.10746
$\eta = \frac{I - A}{2}$ (eV)	2.87667	2.62466	2.42148
$\sigma = \frac{1}{\eta}$	0.347623921	0.3810011491	0.41297058015
$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2\ \eta_{Cu} + \eta_{inh}}$	0.2184	0.15333	0.2834
TE (eV)	-8092.4984	-21930.00890	-9597.968381

Frontier orbital theory is useful in predicting adsorption centres of the inhibitor molecules responsible for the interaction with surface metal atoms [68]. Terms involving the frontier *MO* could provide dominative contribution, because of the inverse dependence of stabilization energy on orbital energy difference [68]. Moreover, the gap between the *HOMO* and *LUMO* energy levels of the molecules was another important factor that should be considered. Reportedly, excellent corrosion inhibitors are usually those organic compounds who not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal [68, 62]. However, in the literature several cases were reported that E_{HOMO}, E_{LUMO} and ΔE_{L-H} did not show direct correlation between these computed quantum chemical values and inhibition efficiencies determined experimentally [74, 75].

In the literature, it is well established that the higher the *HOMO* energy (E_{HOMO}) of the inhibitor, the greater the trend of offering electrons to unoccupied d-orbital of the metal, and the higher the corrosion inhibition efficiency for copper in nitric acid solutions; in addition, the lower the *LUMO* energy, the easier the acceptance of electrons from metal surface, as the *LUMO–HOMO* energy gap decreased, interactions between the reacting species become stronger and as a result efficiency of inhibitor improved. In our study, the values of the *LUMO*, dipole moment (μ) and the total energy (*TE*) energy may be the right tools to interpret the effectiveness of triazoles obtained. The total energy of the best inhibitor *Tz2* is equal to -21930.00890 eV. This result indicated that *Tz2* is favourably adsorbed through the active centers of adsorption and especially the presence of two

groups mercapto and amino on 3 and 4 positions respectively on azole ring. According to Zhang et al. [76] the introduction of mercapto group to a heterocyclic compound can vary the disturbances and orbital energy configurations of electrons, thus enhancing the inhibition. Thus, the higher inhibition effects of *Tz2* in comparison with *Tz3* and *Tz1* may be attributed to the presence of S and N atoms at the same time in its molecular structure. Organic inhibitors which have reactive functional groups are sites of the adsorption process. The strength of the adsorption bond depends upon the electron density of the donor atom. The inhibition efficiency of organic compounds containing different donor atoms is in the sequence [77] S > N > O.

The figure below (Figure 3) shows the distributions of *HOMO* and *LUMO* densities of the three triazoles compounds. Analysis of this figure shows that the density for *Tz1* and *Tz3 LUMO* is mainly localized on the substituent NH_2, by cons for *Tz2*, we note that the distribution *LUMO* is distributed throughout the triazole ring and the three substituents ($-NH_2$,-NH-NH_2 and-SH). However, the distribution of the *HOMO* density of the three triazoles compounds is distributed throughout the triazole ring and on the substituent's of three compounds *Tz1*, *Tz2* and *Tz3*.



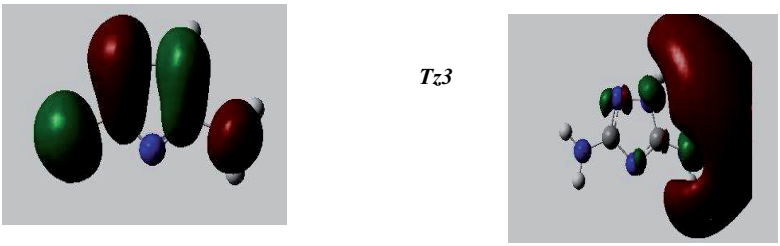


Fig. 3. Schematic representation of *HOMO* and *LUMO* molecular orbital of studied molecules.

Another parameter of the molecular structure is energetic level of (*LUMO*), which determines the polarizability of the compound i.e. the ability to be distorted by an electric field, and hence *LUMO* level receives electrons. In this case, the reaction is characterized with transfer of electrons from the metal to the inhibitor. The calculations also show that *Tz2* has the lowest E_{LUMO}, so it has the greatest ability to interact with the metal surface. The relationship between corrosion inhibition efficiency and *LUMO* energy levels for these three triazoles is plotted in Fig. 4. As clearly seen in the figure, the inhibition efficiency increased with the E_{LUMO} lowest.

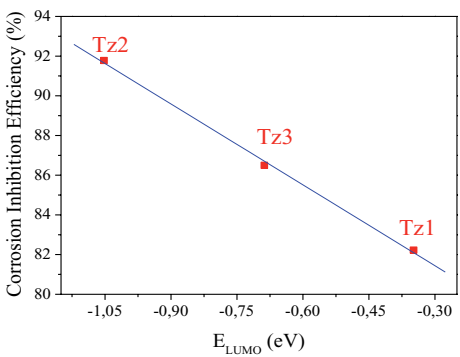


Fig. 4. Correlation of *LUMO* energy with percent inhibition efficiency of Triazoles.

Another quantum chemical parameter such as the dipole moment (μ) was also calculated was the *Tz2* compound has the highest values and accordingly the highest inhibition efficiency. The calculations show that we have the same order of reactivity *Tz2* > *Tz3* > *Tz1*. The high value of μ

probably mean the increase of the adsorption of inhibitor and accordingly increasing the inhibition efficiency [28, 78] which agree with the experimental results. Fig .5 shows the correlation between the dipole moments (μ) and the effectiveness of inhibitory compounds triazoles. We note that increasing this parameter leads to an increase in the efficiency of these compounds inhibiting triazoles.

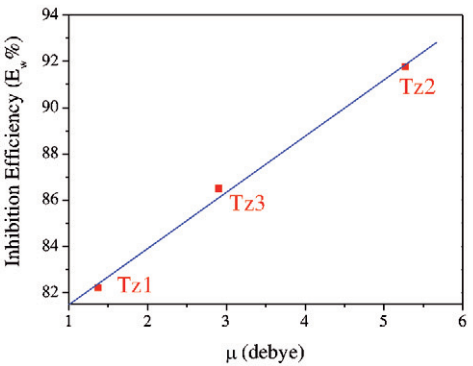


Fig. 5. Correlation between the dipole moments (μ) and the inhibitory efficiencies of triazoles.

In literature it has been reported that the values of ΔN show inhibition effect resulted from electrons donation [60, 57]. According to Lukovits's study [57], if the value of $\Delta N < 3.6$, the inhibition efficiency increased with increasing electron donating ability of inhibitor at the metal surface. Also it was observed [79] that inhibition efficiency increased with increase in the values of ΔN. However, our study reveals that there is no regular trend in the inhibition efficiency by increasing values of ΔN.

The separation energy, $\Delta E = (E_{LUMO} - E_{HOMO})$, is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on metallic surface. As ΔE decreases, the reactivity of the molecule increases leading to increase the inhibition efficiency of the molecule. The values of $\Delta Egap$ for *Tz1*, *Tz2* and *Tz3* are 5.7528, 5.2493 and 4.8429 eV (Table 2), respectively. Even in the literature the correlation between $\Delta Egap$ and inhibition efficiency is often

cited. Our theoretical results indicate that no significant relationship was detected between an *ΔEgap* and inhibition efficiency. Fig 6 summarizes a schematic of diagrams of frontier molecular orbitals for the investigate inhibitors to their estimated energy gap *ΔE*.

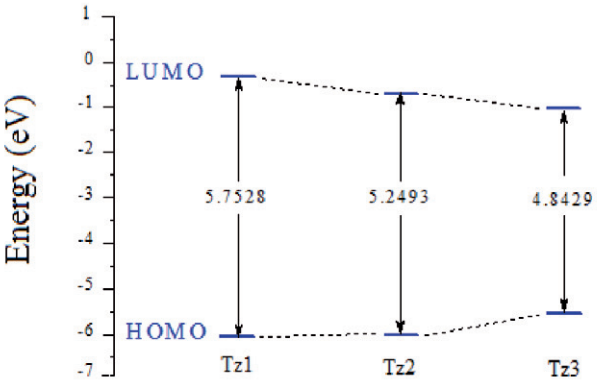


Fig. 6. Correlation diagram of frontier molecular orbitals for the investigated inhibitors and their calculated *ΔE* (eV).

3.4. Conclusion

Using the *DFT/B3LYP* method, the inhibition efficiency of some substituted triazoles is investigated that leads to the following conclusions:

- A good correlation is found between the dipole moment and *IE*. The inhibition efficiency increases with increasing the dipole moment.
- A good correlation is found between the *LUMO* energie and IE. Therefore, the energy of the lowest unoccupied molecular orbital, E_{LUMO}, indicates the ability of the inhibitor molecule to accept electrons. So, the lower the value of E_{LUMO}, the more is the probability the molecule accepts electrons. The inhibition efficiency increases with decreasing of the *LUMO* energy values.

- The total energy of the best inhibitor *Tz2* is the lowest among the compounds studied. This result indicated that *Tz2* is favourably adsorbed through the active centers of adsorption on copper surface.
- There is no direct relationship between the *IE* and the separation energy.

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4 Theoretical Investigation on the Corrosion Inhibition of Copper by Quinoxaline Derivatives in Nitric Acid Solution

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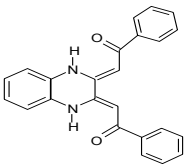
4.1. Introduction

Copper and copper alloys are extensively used in various industry applications, both in aqueous and non-aqueous environments. Copper has found considerable use in the electrotechnical industry due to its high electrical conductivity. The conductivity is, next to the conductivity of silver, the highest electrical conductivity at room temperature of all metals [1]. This high value is due to the mall energy difference between the valence and conduction band allowing electrons to flow freely. Copper does not displace hydrogen from acid solutions and it is therefore unattacked in non-oxidising acid environments. Nevertheless, most acidic solutions contain dissolved air that enables some corrosion to take place. Many organic molecules are used to inhibit copper corrosion [2–6]. The primary step in the action of organic corrosion inhibitors in acid solutions is usually adsorption at the metal–solution interface. The adsorption process depends on the electronic

characteristic of the molecules (adsorbate), the chemical composition of the solution, nature of the metal surface, temperature of the reaction and on the electrochemical potential at the metal–solution interface [7]. The adsorption requires the existence of attractive forces between the adsorbate and the metal. According to the type of forces, adsorption can be physisorption or chemisorption or a combination of both [8]. Physisorption is due to electrostatic attractive forces between inhibiting organic ions or dipoles and the electrically charged surface of the metal. Chemisorption is due to interaction between unshared electron pairs or π electrons with the metal in order to form a coordinate type of bond. The adsorption occurs from active centers such as P, Se, S, N and O atoms, the double or triple bonds and also aromatic rings. The effect of the molecular structure on the chemical reactivity has been subject of great interest in several disciplines of chemistry. The quantum chemical calculations have been widely used to study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities. This is a useful approach to investigate the mechanisms of reaction in the molecule and its electronic structure level and electronic parameters can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry [9]. The advancement in methodology and implementations has reached a point where predicted properties of reasonable accuracy can be obtained from density functional theory (DFT) calculations [10]. The geometry of the inhibitor in its ground state, as well as the nature of their molecular orbitals, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are involved in the properties of activity of inhibitors. The inhibition property of a compound has been often correlated with energy of HOMO, LUMO and HOMO–LUMO gap. The inhibition efficiency of the two inhibitors was studied previously [11].

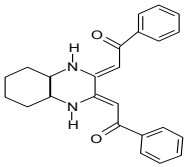
The objective of this paper is to investigate the dependence of inhibition efficiency of these compounds on theoretical chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global

hardness (η), softness (σ), ionization potential (I), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and the total energy (TE). The chemical structures of the compounds studied are given in Fig 1.



(Q5)

(2Z)-2-[(3E)-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1H)-ylidene]-1-phenylethanone



(Q6)

(Z)-2-((E)-3-(2-oxo-2-phenylethylidene)-3,4-dihydroquinoxalin-2(1H)-ylidene)-1-phenylethanone

Fig. 1. The molecular structures of the investigated inhibitors Q5 and Q6.

4.2. Quantum chemical calculations

Complete geometrical optimizations of the investigated molecules are performed using DFT (density functional theory) with the Beck's three parameter exchange functional along with the Lee–Yang–Parr nonlocal correlation functional (B3LYP) [12–14] with 6- 31G* basis set is implemented in Gaussian 03 program package [15]. This approach is shown to yield favorable geometries for a wide variety of systems. This basis set gives good geometry optimizations. The geometry structure was optimized under no constraint. The following quantum chemical parameters were calculated from the obtained optimized structure: The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and the total energy (TE).

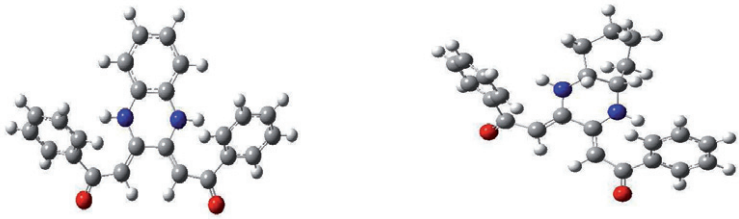
4.3. Results and discussion

The inhibition of copper using substituted quinoxalines as corrosion inhibitors were investigated experimentally. Table 1 indicates clearly a decrease in the corrosion rate in the presence of Q5 and Q6. This effect is hugely marked at higher concentration of inhibitors. The inhibitive action is more explicit by E_I% data which increases with inhibitor concentration to reach 82.9% for Q5, 71.9% for Q6. Quantum chemical calculations have been widely used to study reaction mechanisms. They have also proved to be a very powerful tool for studying corrosion inhibition mechanisms [16]. Recently, theoretical prediction of the efficiency of corrosion inhibitors has become very popular in parallel with the progress in computational hardware and the development of efficient algorithms which assisted the routine development of molecular quantum mechanical calculations [17]. All quantum chemical properties were obtained after geometric optimization with respect to the all nuclear coordinates using Kohn–Sham approach at DFT level. The optimized structure of the studied compound as shown in Fig. 2.

Table 1

Summarized the inhibition efficiency (E_I%) obtained by addition of Q5 and Q6 at different concentrations on the corrosion of copper in 2M HNO_3 solution determined by potentiodynamic polarization [11].

	Conc (M)	E_{corr} (mV/SCE)	$-b_c$ (mV/dec)	I_{corr} (µA/cm^2)	EI (%)
HNO_3	2	34.0	304	365.1	-
	10^{-3}	-04.2	182	062.2	82.9
Q5	10^{-4}	11.8	185	126.2	65.4
	10^{-5}	14.6	167	291.8	20.1
	10^{-6}	15.9	179	328.5	10.0
	10^{-3}	20.1	190	102.5	71.9
Q6	10^{-4}	20.5	190	153.8	57.9
	10^{-5}	25.9	205	290.7	20.4
	10^{-6}	264	193	315.1	13.7



Q5 Q6

Figure 2. Optimized structure of studied molecules obtained by B3LYP/6-31G* level.

The frontier orbital (highest occupied molecular orbital HOMO and lowest unoccupied molecular orbital LUMO) of a chemical species are very important in defining its reactivity. Fukui first recognized this. A good correlation has been found between the speeds of corrosion and E_{HOMO} that is often associated with the electrondonating ability of the molecule. Survey of literature shows that the adsorption of the inhibitor on the metal surface can occur on the basis of donor–acceptor interactions between the π-electrons of the heterocyclic compound and the vacant d-orbital of the metal surface atoms [18], high value of E_{HOMO} of the molecules shows its tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbitals. Increasing values of E_{HOMO} facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. Similar relations were found between the rates of corrosion and ΔE ($\Delta E = E_{LUMO} - E_{HOMO}$) [19–21]. The energy of the lowest unoccupied molecular orbital indicates the ability of the molecule to accept electrons. The lower the value of E_{LUMO}, the more probable the molecule would accept electrons. Consequently, concerning the value of the energy gap ΔE, larger values of the energy difference will provide low reactivity to a chemical species. 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 [22]. Another method to correlate inhibition efficiency with parameters of molecular structure is to calculate the fraction of electrons transferred from inhibitor to metal surface. According to Koopman's theorem [23], E_{HOMO}

and E_{LUMO} of the inhibitor molecule are related to the ionization potential (I) and the electron affinity (A), respectively. The ionization potential and the electron affinity are defined as I = - E_{HOMO} and A = - E_{LUMO}, respectively. Then absolute electronegativity (χ) and global hardness (η) of the inhibitor molecule are approximated as follows [22]:

$$\chi = \frac{I + A}{2} \qquad (1)$$

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

The global electrophilicity index was introduced by Parr [24] and is given by:

$$\omega = \frac{\mu^2}{2\eta} \qquad (3)$$

Thus the fraction of electrons transferred from the inhibitor to metallic surface, ΔN, is given by [25]:

$$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2\ (\eta_{Cu} + \eta_{inh})} \qquad (4)$$

In order to calculate the fraction of electrons transferred, a theoretical value for the electronegativity of bulk copper was used χ_{Cu}= 4.48 eV/mol [23], and a global hardness of , η_{Cu} = 0 eV/mol by assuming that for a metallic bulk $I = A$ [26] because they are softer than the neutral metallic atoms.

Quantum chemical parameters obtained from the calculations which are responsible for the inhibition efficiency of inhibitors, such as the highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), HOMO–LUMO energy gap ($\Delta E_{H\text{-}L}$), dipole moment (μ) and total energy (TE), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), The global electrophilicity (ω), the fraction of electrons transferred from the inhibitor to iron surface (ΔN) and the total energy (TE) , are collected in Table 2.

Table 2

Calculated quantum chemical parameters of the studied compounds.

Quantum parameters	Q5	Q6
E_{HOMO} (eV)	-5.4378	-5.540
E_{LUMO} (eV)	-2.17812	-1.964
ΔE gap (eV)	3.259	3.576
μ (debye)	8.1609	9.6768
EI (%)	82.9	71.9
$I = -E_{HOMO}$ (eV)	5.4378	5.540
$A = -E_{LUMO}$ (eV)	2.17812	1.964
$\chi = \frac{I + A}{2}$ (eV)	3.80796	3.752
$\eta = \frac{I - A}{2}$ (eV)	1.62984	1.788
$\sigma = \frac{1}{\eta}$	0.61356	0.55928
$\omega = \frac{\mu^2}{2\eta}$	20.43154	26.18581
$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2\ \eta_{Cu} + \eta_{inh}}$	0.54766	0.65083
TE (eV)	-1185.3283101	-1188.9302589

In Fig. 3, we have presented the frontier molecule orbital density distributions of the studied compounds: HOMO (right); LUMO (left). Analysis of Fig. 3 shows that the distribution of two energies HOMO and LUMO, we can see that the electron density of the HOMO location in the Quinoxaline molecules is mostly distributed near the nitrogen (NH) and oxygen (= O) atoms and quinoxaline ring indicating that these are the favorite sites for adsorption, while the density LUMO was distributed almost of the entire molecules.

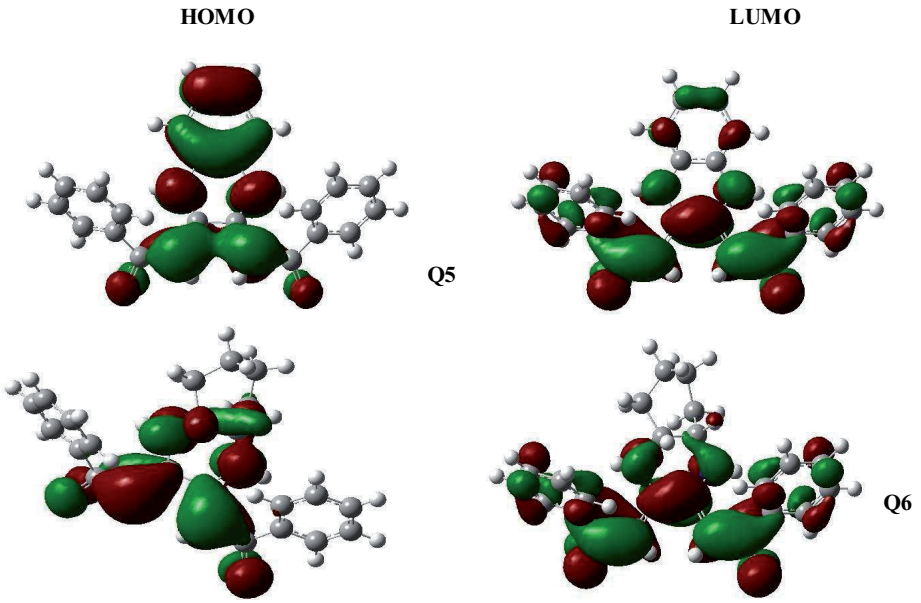


Fig. 3. Schematic representation of HOMO and LUMO molecular orbital of studied molecules.

According to the frontier molecular orbital theory (FMO) of chemical reactivity, transition of electron is due to interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species [27]. E_{HOMO} is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [28]. The inhibitor does not only donate electron to the unoccupied d orbital of the metal ion but can also accept electron from the d-orbital of the metal leading to the formation of a feedback bond. The highest value of E_{HOMO} -5.4378 (eV) of **Q5** indicates the better inhibition efficiency.

It has also been found that an inhibitor does not only donate an electron to the unoccupied d orbital of the metal ion but can also accept electrons from the d orbital of the metal leading to the formation of a feedback bond. Therefore, the tendency for the formation of a feedback bond would

depend on the value of E_{LUMO}. The lower the E_{LUMO}, the easier is the acceptance of electrons from the d orbital of the metal [21]. Based on the values of E_{LUMO}, the order obtained for the decrease in inhibition efficiency (Q5 > Q6) was also similar to the one obtained from experimental results.

The separation energy, $\Delta E = E_{LUMO} - E_{HOMO}$ is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on metallic surface. As ΔE decreases, the reactivity of the molecule increases leading to increase the inhibition efficiency of the molecule. The results obtained from quantum chemical calculation are listed in Table 2. The calculations indicate that Q5 has the lowest value which means the highest reactivity among the other inhibitor and accordingly the highest inhibition efficiency which agrees well with the experimental observations. The order of reactivity in this case will be:

Q5 > Q6.

Absolute hardness and softness are important properties to measure the molecular stability and reactivity. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [29]. In our present study **Q5** with low hardness value 1.62984 (eV) compared with other compound have a low energy gap. Normally, the inhibitor with the least value of global hardness (hence the highest value of global softness) is expected to have the highest inhibition efficiency [30]. For the simplest transfer of electron, adsorption could occur at the part of the molecule where softness (σ), which is a local property, has a highest value [19]. Q5 with the softness value of 0.61356 has the highest inhibition efficiency.

The most widely used quantity to describe the polarity is the dipole moment of the molecule [31]. Dipole moment is the measure of polarity of a polar covalent bond. It is defined as the product of charge on the atoms and the distance between the two bonded atoms. The total dipole moment, however, reflects only the global polarity of a molecule. For a complete molecule the total molecular dipole moment may be approximated as the vector sum of individual bond dipole

moments. The dipole moment (μ in Debye) is another important electronic parameter that results from non uniform distribution of charges on the various atoms in the molecule. The high value of dipole moment probably increases the adsorption between chemical compound and metal surface [32]. The energy of the deformability increases with the increase in μ, making the molecule easier to adsorb at the Cu surface. The volume of the inhibitor molecules also increases with the increase of μ. This increases the contact area between the molecule and surface of copper and increasing the corrosion inhibition ability of inhibitors. In our study, there is no direct relationship between the E_I(%) and the dipole moment.

In literature it has been reported that the values of ΔN show inhibition effect resulted from electrons donation [23, 33]. According to Lukovits's study [33], if the value of $\Delta N < 3.6$, the inhibition efficiency increased with increasing electron donating ability of inhibitor at the metal surface. Also it was observed [34] that inhibition efficiency increased with increase in the values of ΔN. However, our study reveals that there is no regular trend in the inhibition efficiency by increasing values of ΔN.

The total energy calculated by quantum chemical methods is also a beneficial parameter. The total energy of a system is composed of the internal, potential, and kinetic energy. Hohenberg and Kohn [35] proved that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy. In our study the total energy of the best inhibitor Q5 is equal to -1185.3283101 eV, this value is lower than that of the compound Q6.

Analysis of charge repartition of compounds Q5 and Q6

The comparison of the reparation atomic charge (Fig. 4) of Q5 and Q6 shows no evident and apparent difference but the look for lowest energy conformer of Q5 and Q6 lead us to conformers1 which have respective energy of 97.02 and 92.38 Kcal/mol (Fig. 5).

Crystalline structure analysis of compound Q5

The crystalline structure of Q5 (Fig. 6) is fully in agreement with the structures proposed for conformer 1 with lowest energy. The molecule is quasi-planar [36] with a C symmetry axis: the external phenyl rings are twisted by 25 °.

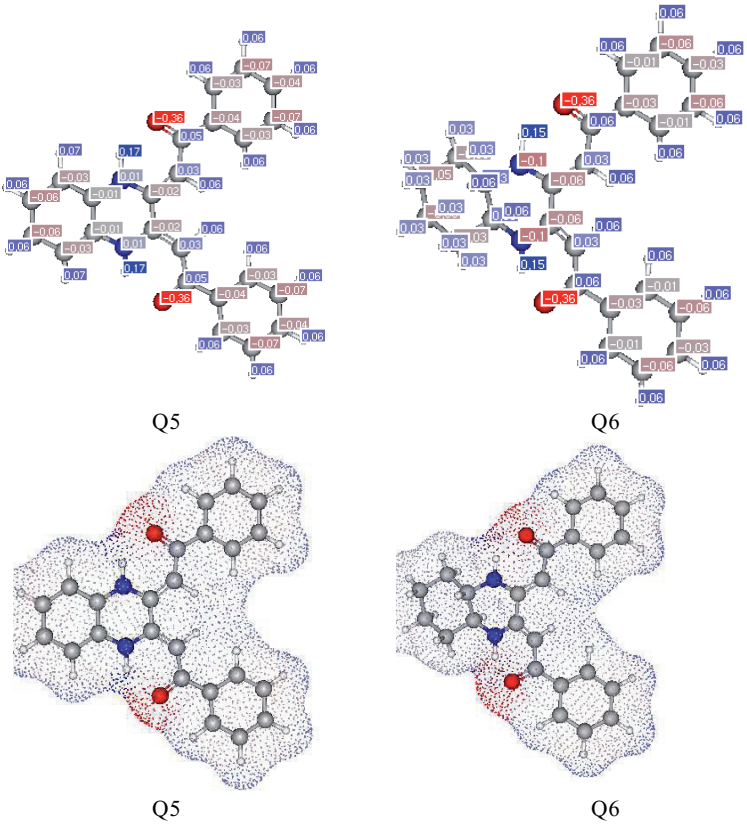


Fig. 4. Charge repartition of quinoxalines Q5 and Q6.

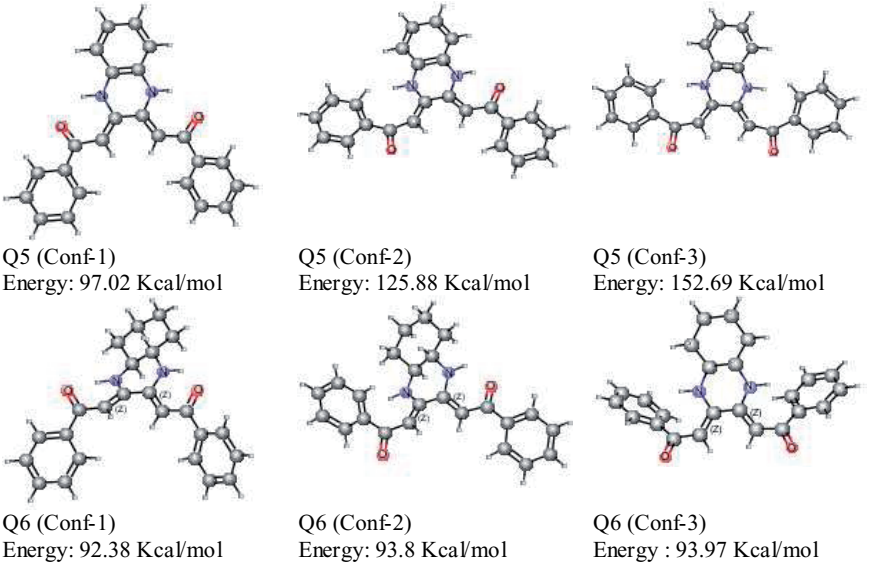


Fig. 5. Lowest and highest energy conformers of quinoxalines Q5 and Q6.

The nitrogen atom N(1) is trivalent with an N(1)-H(1) bond length of about 0.88 A, confirming the position of the acidic proton. In addition, N(1), C(2), C(8a) and H(1) are perfectly coplanar, resulting from the sp2 hybridization of the nitrogen atom due to the conjugation with the delocalized pi-system. The C(9)-C(10) and C(2)-C(3) distances [1.431(2) and 1.482(3) A, respectively] lie in between single and double bond lengths, confirming the high electronic delocalization. The H(1) --- O(1) distance of about 1.8 A. and the N(1), H(1), O(1) angle of ca. 15°, suggests an intra-molecular N(1)-H(1) --- O(1) hydrogen bond in accordance with the strong NMR deshielding of H(1) [15.0 ppm].[37]

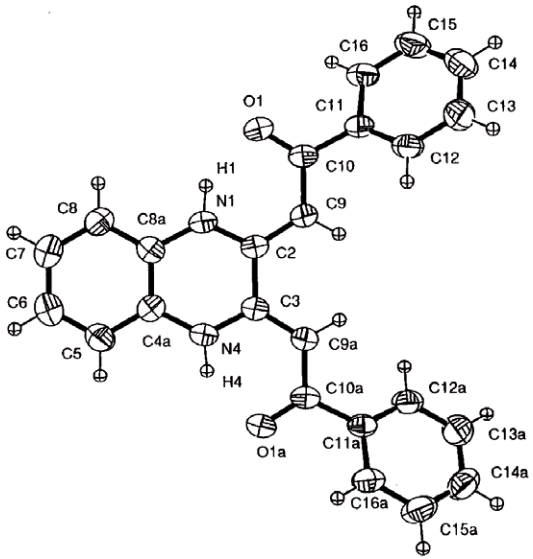


Fig. 6. ORTEP drawing of compound **Q5**.

4.4. Conclusion

The correlation between the quantum chemical parameters and inhibition efficiency of some quinoxaline compounds was investigated using DFT/B3LYP calculations. The inhibition efficiency of the inhibitor are closely related to the quantum chemical parameters, the highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), HOMO–LUMO energy gap (ΔE_{H-L}), the hardness (σ), the softness (η) and the fraction of electrons transferred (ΔN) for the neutral inhibitors and no significant relationship was found with parameters, dipole moment (μ) and the total energy (TE).

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5 Theoretical Study of the Corrosion Inhibition of some Bipyrazolic Derivatives A Conceptual DFT Investigation

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5.1. Introduction

The polypyrazolyl compounds are most thoroughly studied in organic chemistry. Some of these compounds were synthesized for industrial, biological, and medicinal aims. Moreover, the pyrazolic compounds are regarded as good agents not only for their affinity to complex the alkalines cations [1], but also to form stable complexes with the ions of transition metals [2]. These complexes are so stable that it is often difficult to obtain a free ligand.

Copper or iron and their alloys corrosion inhibition via pyrazole, triazole, imidazole and tetrazole derivatives rank as extensively researched topic [3-6]. The inhibition efficiency of such inhibitors depends essentially on the structure of the inhibitor itself, which includes the number of adsorption active centers in the molecule, the nature of the metal and the aggressive solution. The structure and the lone electron pairs in the heteroatoms are important features that determine the adsorption of these molecules on the metallic surface.

The inhibition efficiency has been found to be closely related to inhibitor adsorption abilities and molecular properties for different kinds of organic compounds [7-9].

The corrosion inhibition of metals trough organic compounds has been the subject of different theoretical investigations. Khaled [10], realized a correlation between experimental efficiencies of inhibitors and the results of quantum chemical calculations, and constructed a composite index

of some of the key quantum chemical parameters in order to characterize the inhibition performance of the tested molecules. Khalil et al. [11] studied the structural effects of polymethylene amines on corrosion inhibition of iron in acid solutions. Hong et al. performed a quantum chemical calculations based on DFT methods on three polydentate Schiff base compounds and calculated some global quantities which are correlated with inhibition efficiencies [12]. Taner et al. [13] studies the corrosion inhibition of some sulphonamides on mild steel by means of quantum chemical calculations.

Recently, it has been shown that the study of the chemical responses of molecular systems under external perturbation may be significantly facilitated if reliable scales of electrophilicity and nucleophilicity are available. The utility of such global and local reactivity scales is of great importance to answer some fundamental questions in chemistry such as reaction feasibility (whether or not a given reaction will take place). An excellent source that illustrates this concept well is the review work published by Mayr et al.[14] The development of theoretical scales of electrophilicity and nucleophilicity on the other hand is also desirable as a validated theoretical scale may be further used to project the global reactivity onto particular regions on the molecule. There are different ways to model the electrophilicity concept using the electronic structure of molecules. A suitable one is that based on Parr et al.'s definition of global electrophilicity [15]. The best descriptors for studying local reactivity and regioselectivity will be the local electrophilicity and the local nucleophilicity. Very recently, Domingo et al. introduced the global and local (regional) nucleophilicity indices [16,17].

Dafali et al. [18] has studied the corrosion inhibition efficiency of some bipyrazolic coumponds (L1) *N,N*-(bis((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl))ethanolamine; (L2)*N,N*-(bis((3,5-dimethyl-1*H*-pyrazol-1-yl) methyl) allyl amine; (L3)*N,N*-(bis((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)butylamine ; (L4) *N,N*-(bis((3,5-dimethyl-1*H*-pyrazol-1-yl)methyl)cyclohexylamine ; (L5) *N,N*-(bis((3-carbomethoxy-5-methyl-1*H*-pyrazol-1-yl)methyl)cyclohexylamine ; (L6) *N,N*-(bis((3-carboethoxy-5-methyl-1*H*-pyrazol-1-

yl)methyl)cyclohexylamine of copper in 3 per cent NaCl solution using both electrochemical polarization and weight loss techniques and found that all the examined bipyrazolic compounds reduce the corrosion of copper. The above study conditions were done by analogy of sea water effect on copper. The use of bipyrazolic compounds and their derivatives as good inhibitors can be explained by the presence of five atoms of nitrogen in the molecule. these has a major effect on the inhibition efficiencies and consequently on the adsorption phenomenon on the metal surface in addition to their large molecular surface which induces a widespread covering of the surface of the metal (copper) [18].

Our aim in this work is to give a deeper insight on the substituent effect on the inhibition efficiency of L1, L2, L3, L4, L5 and L6 compounds (Scheme1) using DFT-based reactivity indexes.

Scheme. 1. Molecular structure of the studies bypirazolic compounds

5.2. Theoretical Background

5.2.1. Global quantities

Popular qualitative chemical concepts such as electronegativity [19] (χ) and hardness [20] (η) have been provided with rigorous definitions within the purview of conceptual density functional theory [21,22] (DFT). Electronegativity is the negative of chemical potential defined [23] as follows for an N-electron system with total energy E and external potential $v(\vec{r})$.

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

μ is the Lagrange multiplier associated with the normalization constraint of DFT [21,24].

Hardness (η) is defined [25] as the corresponding second derivative,

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

Using a finite difference method, working equations for the calculation of χ and η may be given as [21]:

$$\chi = \frac{I + A}{2} \tag{3}$$

$$\eta = I - A \tag{4}$$

where I and A are the ionization potential and electron affinity, respectively. If ε_{HOMO} and ε_{LUMO} are the energies of the highest occupied and lowest unoccupied molecular orbitals, respectively, then the above equations can be rewritten, [26]using Koopmans' theorem [27], as

$$\chi = -\frac{\varepsilon_{HOMO} + \varepsilon_{LUMO}}{2} \tag{5}$$

$$\eta = \varepsilon_{LUMO} - \varepsilon_{HOMO} \tag{6}$$

2.2 Local quantities:

Local quantities such as Fukui function $f(r)$ and local softness $s(r)$ defined the reactivity/selectivity of a specific site in a molecule. 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 $v(r)$ [28].

$$f(r) = \left[\frac{\partial \rho(r)}{\partial N}\right]_{v(r)} = \left[\frac{\delta \mu}{\delta v(r)}\right]_{N} \qquad (7)$$

Using left and right derivatives with respect to the number of electrons, electrophilic and nucleophilic Fukui functions for a site k in a molecule can be defined [29].

$$f_k^{+} = \rho_k(N+1) - \rho_k(N) \qquad \text{for nucleophilic attack} \qquad (8a)$$

$$f_k^{-} = \rho_k(N) - \rho_k(N-1) \qquad \text{for electrophilic attack} \qquad (8b)$$

$$f_k^{0} = \rho_k(N+1) - \rho_k(N-1)/2 \qquad \text{for radical attack} \qquad (8c)$$

Where $\rho_k(N)$, $\rho_k(N-1)$ *and* $\rho_k(N+1)$ are the gross electronic populations of the site k in neutral, cationic, and anionic systems, respectively.

One of the practical problems for the interpretation of the condensed Fukui function is the existence of negative values [30, 31].

2. 3. Domingo's definition of global and local nucleophilicity indexes:

2. 3. 1. The global nucleophilicity indexe N:

According to Domingo et al. [16, 17], the global nucleophilicity index, *N*, is defined by the following formula:

$$N = \varepsilon_{HOMO(Nu)} - \varepsilon_{HOMO(TCE)} \quad (in\ eV\ units) \qquad (10)$$

Where $\varepsilon_{HOMO(Nu)}$ is associated to the HOMO energy within the Kohn–Sham scheme [32] and $\varepsilon_{HOMO(TCE)}$ corresponds to the HOMO energy of the tetracyanoethylene (TCE) taken as reference. Satisfactory linear correlation has been found between experimental ionization potentials and calculated nucleophilicities for a large series of molecules.

2. 3.2. The local nucleophilicity indexe N_k:

The global nucleophilicity index (N) can be expressed as the sum of local nucleophilicities condensed to all atoms of the molecule:

$$N = \sum N_k \quad (11)$$

From the above definition of the global nucleophilicity, it is possible to define the local nucleophilicity condensed to an atom k through the nucleophilic Fukui function, f_k^-, [17].

$$N_k = N f_k^- \quad (12)$$

5.2.2. Calculation methods

The quantum chemical calculations reported in this work are performed, at the B3LYP/6-31G (d) level of theory, using GAUSSIAN 03 series of programs [33]. The optimizations of equilibrium geometries of all reactants were performed using the Berny analytical gradient optimization method [18]. The electronic populations as well as the Fukui indices and local nucleophilicities are computed using different populations analysis MPA (Mulliken population analysis), NPA (natural population analysis) [35]. The cationic systems, needed in the calculation of nucleophilic Fukui indices are taken in the same geometry as the neutral system.

5.3. Results and discussion

5.3.1. Relationships between inhibition efficiency and the global quantum chemical parameters

The inhibition efficiency of the compounds depends on many major factors such as the number of adsorption active centers in the molecule and their charge density, molecule size, mode of adsorption and formation of metallic complex.

The substitute effect on the copper inhibition of the bipyrazol compounds L1 to L6 will be rationalized using global reactivity indexes, namely, the nucleophilicity index *N*, the electronic chemical potential, the hardness and the HOMO/LUMO gaps. The algebraic values of this quantity are given in (Tables 1and 2).

Table 1

HOMO and LUMO energies, HOMO-LUMO gaps, Electronic chemical potentials μ, nucleophilicity indices *Nu*, Hardness η, and The maximum electronic charge ΔN_{max} for compounds L1-L6.

Compound	R_2	R_1	HOMO (au)	LUMO (au)	μ (au)	η (au)	ΔN_{max}	*Nu* (eV)	Gap (a.u)	% IE
L1	CH_2CH_2OH	CH_3	-0.2223	0,0191	-0,1016	0,241	0,42	3,31	-0,2414	99,5
L2	CH_2CHCH_2	CH_3	-0,2208	0,0212	-0,0999	0,242	0,41	3,35	-0,2420	99
L3	C_4H_9	CH_3	-0,2202	0,023	-0,0986	0,243	0,40	3,37	-0,2432	99,4
L4	C_6H_{11}	CH_3	-0,2175	0,0270	-0,0953	0,244	0,38	3,44	-0,2445	98,9
L5	C_6H_{11}	CO_2CH_3	-0,2250	-0,0303	-0,1277	0,194	0,65	3,24	-0,1948	94,4
L6	C_6H_{11}	$CO_2C_2H_5$	-0,2252	-0,0290	-0,1271	0,196	0,64	3,23	-0,1964	94,6

[a] *The HOMO energy, -0.34426 a.u, of the reference system (TCE) has been calculated at the same computational level.*

[b] *IE%= (1-I/I$_0$).100 where I$_0$ and I are the corrosion current density values without and with inhibitor, respectively.*

Table 2

HOMO-1 and LUMO energies, HOMO-1-LUMO gaps, Electronic chemical potentials μ, nucleophilicity indices *Nu*, Hardness η, and The maximum electronic charge ΔN_{max} for compounds L1-L6.

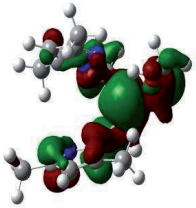
Compound	R_2	R_1	HOMO-1 (au)	LUMO (au)	μ (au)	η (au)	ΔN_{max}	N (eV)	Gap (a.u)	% IE
L1	CH_2CH_2OH	CH_3	-0,2247	0,0191	-0,1028	0,243	0,42	3,25	-0,2438	99,5
L2	CH_2CHCH_2	CH_3	-0,2260	0,0212	-0,1024	0,247	0,41	3,21	-0,2472	99
L3	C_4H_9	CH_3	-0,2244	0,0230	-0,1007	0,247	0,40	3,26	-0,2474	99,4
L4	C_6H_{11}	CH_3	-0,2217	0,0270	-0,0973	0,248	0,39	3,33	-0,2487	98,9
L5	C_6H_{11}	CO_2CH_3	-0,2358	-0,0303	-0,1330	0,205	0,64	2,95	-0,2055	94,4
L6	C_6H_{11}	$C0_2C_2H_5$	-0,2362	-0,0290	-0,1326	0,207	0,63	2,93	-0,2073	94,6

According to the nature of R_1 and R_2 substituents, the bipyrazol compounds were classified in two classes (a: L1 to L4 and b: L5 and L6). The inhibition of these compounds was determined experimentally by using both electrochemical polarization and weight loss techniques, and was found to be excellent inhibitors of copper corrosion [18]. The slight decrease in the inhibition efficiency observed between L1, L2, L3, L4 and L5, L6 is due to an effect of R_1. It is worth noting that experiment show that the substituted fixed on the nitrogen of the amine has not much effect on the inhibition efficiency.

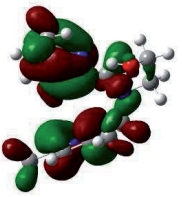
It is noted that the choice of a given molecular orbital (MO) to rationalize the chemical reactivity. It should be certainly necessary the previous knowledge of the particular MO shape [16].

After visualization of molecular orbitals calculated by the method B3LYP/6-31G (d) (See the distribution of electron density of frontier orbitals HOMO, HOMO-1 in Figure 1), it was concluded that the HOMO of these compounds bipyrazolic does not match the aromatic π system of the two pyrazole rings, but rather to the other fragments of molecules. However, it was been Shawn experimentally that the tow nitrogen atoms in the cyclic rings and the various substituted are the major active centers of the adsorption. Indeed, the HOMO of these compounds does not contribute to explain their efficiency inhibition but the HOMO-1 can do this role. In these cases, analysis of the effectiveness of inhibition is based on the energy gaps (HOMO-1-LUMO). The chemical potential and nucleophilicity were estimated using the HOMO-1 and the LUMO (see Figure 1 and Table 2). However, the gap between the HOMO-1 and LUMO molecules is an important factor that should be considered. The excellent corrosion inhibitors are generally organic compounds that not only donate electrons to the unoccupied orbitals of the metal, but also accept free electrons of the metal.

L1

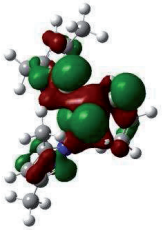


HOMO

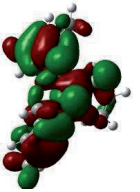


HOMO-1

L2

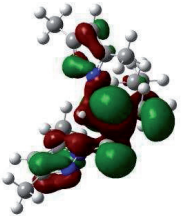


HOMO

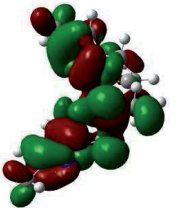


HOMO-1

L3

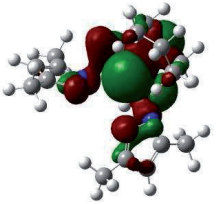


HOMO

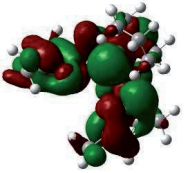


HOMO-1

L4

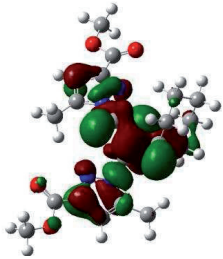


HOMO

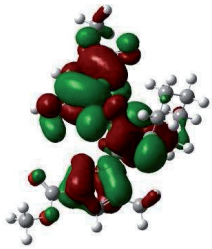


HOMO-1

L5

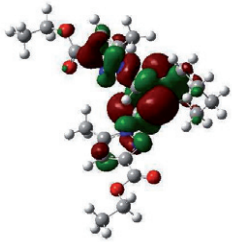


HOMO

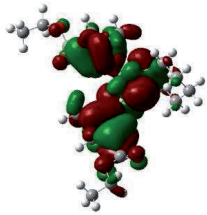


HOMO-1

L6



HOMO



HOMO-1

Fig. 1. Calculated HOMO and HOMO-1 molecular orbitals of the studied molecule L1-L6 using B3LYP/6-31G method.

By analyzing the HOMO-1-LUMO energy gaps values for these bipyrazolic compounds (table 2), it can be noted that:

For compounds L1-L4, the HOMO-1-LUMO energy gaps values are lower than those obtained for L5-L6 compounds. Therefore, the L1-L4 compounds (substituted by electrondonating groups) are predicted to be better corrosion inhibitors gaps HOMO-1-LUMO (L1: -0,2438, L2: -0,2472, L3: -0,2474, L4: -0,2487)a.u. than the L 5-L6 compouds (substituted by electronwithdrawing groups) (L5: -0,2055, L6: -0,2073)a.u. These results are in total agreement with the experimental results.

The HOMO-1-LUMO energy gaps these species is consistent with the calculated electronic chemical potentials, μ and the global nucleophilicity indexes showing that L1 μ=-0,1028a.u.;

N=3,01eV; L2 μ=-0,1024a.u.; N=2,97eV, L3 μ=-0,1007a.u.; N=3,01eV and L4 μ=-0,0973a.u.; N=3,09eV are characterized by the highest chemical potential and global nucleophilicity compared to, L5 μ=-0,1330a.u.; N=2,70eV and L6 μ=-0,1326a.u.; N=2,69eV.

4.2. Relationships between inhibition efficiency and the local quantum chemical parameters:

The energy levels of frontier orbitals indicate the tendency to form bonds to the metal surface. Further study on chelation centers inhibitors requires information on the spatial distribution of electron density of these compounds [16]. The structure of molecules can affect the adsorption by influencing the electron density of the functional group. In order to rationalize the local reactivity, we have calculated the local nucleophilicity indices N_k . The results are summarized in Table 3.

Table 3

Fukui functions values, f_k^-, locals nucleophilicity indexes N_k: of the sites N_1, N_2, N_3, N_4, N_5 for L1-L6 systemes and O for L1.

Indexes	N_1		N_2		N_3		N_4		N_5		O	
Compound	f_k^-	N_k	f_k^-	N_k	f_k^-	N_k	f_k^-	N_k	f_k^-	N_k	f_k^-	N_k
L1	0,1672	0,50	-0,0084	-0,03	0,0356	0,11	0,0053	0,02	0,0760	0,23	0,043	0,13
L2	0,4317	1,28	0,0864	0,26	0,2790	0,83	0,0896	0,27	0,2743	0,81		
L3	0,1307	0,39	-0,0096	-0,03	0,1054	0,32	-0,0158	-0,05	0,0663	0,20		
L4	0,1336	0,41	-0,0121	-0,04	0,0987	0,30	-0,0043	-0,01	0,0749	0,23		
L5	0,2578	0,70	0,0029	0,01	-0,0170	-0,05	-0,0139	-0,04	0,0585	0,16		
L6	0,2536	0,68	0,0120	0,03	-0,0255	-0,07	-0,0194	-0,05	0,0601	0,16		

The local nucleophilicity indexes, N_k is calculated using natural population analyses (NPA).

The analysis of the local nucleophilicity indices given in Table 3 show that:

The central nitrogen atom and the oxygen atom in the case of L1 positions are characterized by the highest value of the local nucleophilicity indice. As a result, the atoms N, O and C atoms of the pyrazole ring are the most reactive centers, which have the greatest ability to bind to the metal surface. On the other hand, the HOMO-1 (Fig. 1) is important in the area containing five nitrogens.

We conclude that this area is the region of reactive centers that transfers electrons from nitrogen to the copper surface.

5.3.2. Correlations between quantum calculated parameters and experimental inhibition efficiency

As a second part of our paper we will give a correlation between the theoretical calculated parameters and the experimental corrosion inhibition efficiency (%IE) . In Fig2-6 we plot the (%IE) versus the LUMO, electronic chemical potential, nucleophilicity, (HOMO-1-LUMO) energy gap and HOMO-1, for these six bipyrazolic compounds. Good linear correlations were obtained with good regression coefficients (R^2) in all cases (correlation coefficient $R^2 > 0.96$).

Consequently, we can conclude that the corrosion inhibition efficiency become better when the system is caracterised by a high values of the electronic chemical potential, HOMO-1 energy, LUMO energy, nucleophilicity and low values of the HOMO-1-LUMO energy in other word the efficiency of inhibition varies proportionally with E_{HOMO-1}, E_{LUMO}, N and μ, however, it is inversely proportional to (E_{HOMO-1}-E_{LUMO}) energy gap.

On the other hand, we used multiple regressions (MLR) to obtain the best correlationsbetween IE% and more than one parameter. The best correlation with experimental IE% (R^2 = 0.997) is obtained using the three variables E_{LUMO}, μ and the gap with a good statistical parameter (Fisher test, p value, Student t-test, the error -SD). The equation of multiple linear regression (MLR) of this model is:

%IE = 160 + 27439 LUMO - 27160 μ +13850 gap

(R^2=0.997, SD=0.20, Fisher-test=253.15, p-value < 0.05, t-test >2)

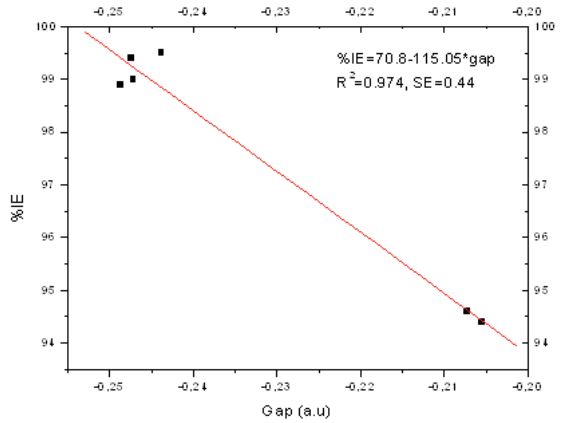


Fig.2. Correlation of LUMO energy with percent inhibition of L1-L6

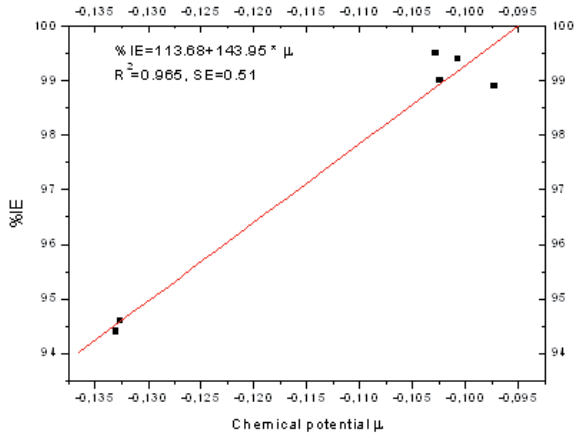


Fig.3. Correlation of of chemical electronic potential μ with percent inhibition of L1-L6

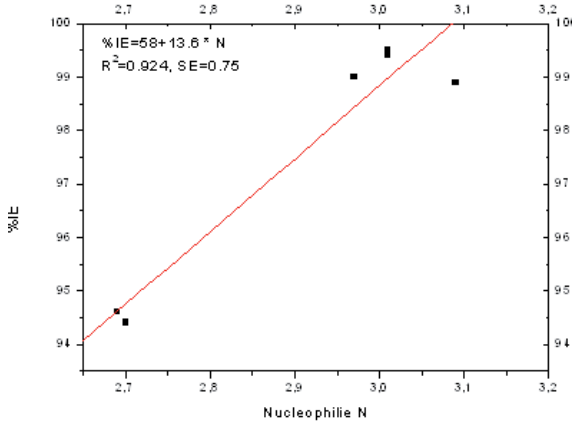


Fig.4. Correlation of nucleophilicity N gaps with percent inhibition of L1-L6

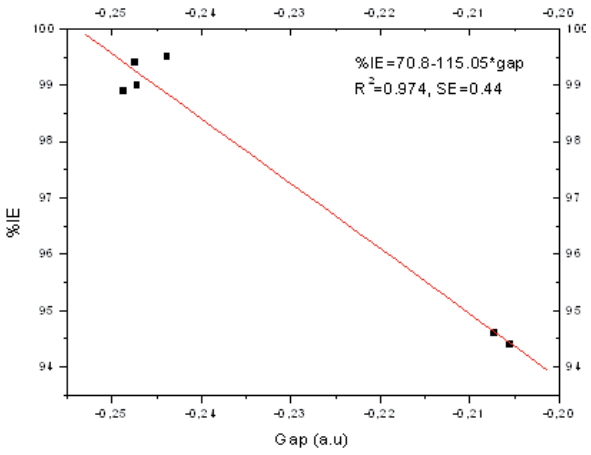


Fig.5. Correlation of E_{HOMO-1}-E_{LUMO} energy gaps with Percent inhibition of L1-L6

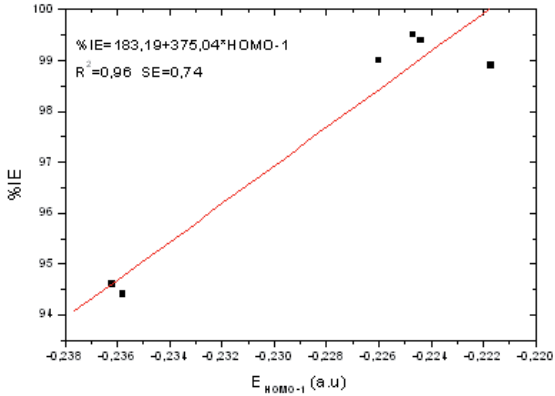


Fig.6. Correlation of HOMO-1 energy with percent inhibition of L1-L6

5.4. Conclusion

Tripods bipyrazoliques studied are effective for inhibiting corrosion of copper in a solution of 3% NaCl. In comparing the percentages of inhibition efficiency (%IE) of the studied compounds with the theoretical results, we note that their inhibitory effects are closely related to E_{HOMO-1}, gap (E_{HOMO}-1-E_{LUMO}) nucleophilicity (N) and the electronic chemical potential (μ). These parameters were calculated by DFT method. The % IE increases when E_{HOMO-1}, N and μ increase, and when the gap (E_{HOMO-1}-E_{LUMO}) decreases. Therefore, compounds L1-L4 are better corrosion inhibitors (presence of donor groups on the pyrazole ring), that L5-L6 (presence of withdrawing groups on the pyrazole ring). The quantum chemical calculations indicate that it is not convenient to consider a single parameter. However, several parameters were considered to characterize the inhibitory activity of the molecules.

The local indices nucleophilicity N_K of the series of bipyrazolic compounds were discussed in a simple but precise purpose. The distribution of the electron density shows that the compounds studied had many active centers in nucleophilicity. The areas containing the nitrogen atoms have more opportunity to form bonds with the copper surface, by donating electrons to the metal.

However, sites N1, N3 and N5 are most favorable for electrophilic attack, in addition to oxygen, in the case of L1. It is interesting to note that the substituent attached to the amine nitrogen has little effect on the efficiency of inhibition, unlike the effect of substituent on the pyrazole ring. This is in perfect agreement with experiment.

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General conclusion

The accuracy of results from DFT calculations can be poor to fairly good, depending on the choice of basis set and density functional. The choice of density functional is made more difficult because creating new functionals is still an active area of research. At the time of this book's publication, the B3LYP hybrid functional (also called Becke3LYP) was the most widely used for molecular calculations by a fairly large margin. This is due to the accuracy of the B3LYP results obtained for a large range of compounds, particularly organic molecules. However, it would not be surprising if this functional's dominance changed within a few years. At the present time, DFT results have been very good for organic molecules, particularly those with closed shells. Quantum chemical calculations based on DFT/B3LYP level are performed to find the relation between the molecular structure of the inhibitor and the inhibition efficiency. The role of quantum chemistry in corrosion inhibitor studies is likely to increase in the future, as the focus of investigations shifts toward complicated chemical mechanisms. However, the restrictions caused by the high computational effort of the calculations mean that quantum chemical methods will not in the foreseeable future be able to replace experimental corrosion studies or computationally less expensive methods for the processes related to corrosion inhibition. In the present book DFT quantum chemical calculations a correlation between parameters related to the electronic structure of some cyclic nitrogen compounds and their ability to inhibit the corrosion process could be established. Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

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