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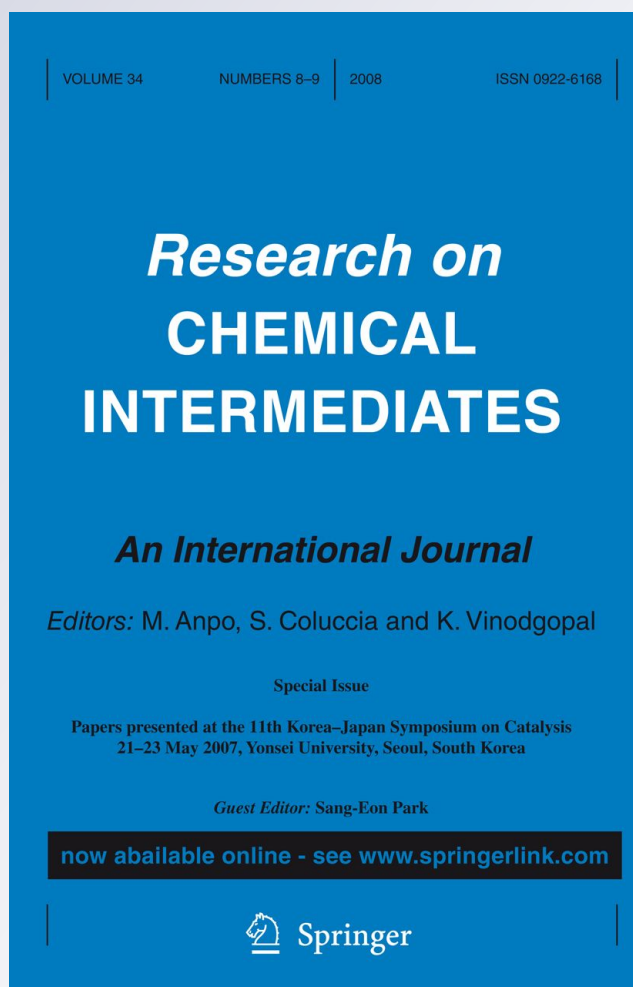
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# Theoretical study of the corrosion inhibition of some bipyrazolic derivatives: a conceptual DFT investigation

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**Abstract** Corrosion inhibition of copper through six bipyrazolic compounds has been elucidated by means of density functional theory (DFT)-derived reactivity indexes. The DFT calculated parameters and experimental corrosion inhibition efficiency (IE%) indicate that their inhibition effect is closely related to the frontier orbital energies, polarizability, electronic chemical potential and global nucleophilicity. The quantum chemistry calculations were performed at the B3LYP/6-31G (d) level. The theoretical results, predicted using DFT-based reactivity indexes, are in good agreement with experimental outcomes.

**Keywords** Bipyrazole · DFT-derived indices · Hardness · Nucleophilicity · Corrosion inhibition

## Introduction

The polypyrazolyl compounds are very thoroughly studied in organic chemistry. Some of these compounds have been 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

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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 an 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 active adsorption 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 through 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. [8] studied the structural effects of polymethylene amines on corrosion inhibition of iron in acid solutions. Hong et al. [11] performed quantum chemical calculations based on DFT methods on three polydentate Schiff base compounds, and calculated some global quantities which are correlated with inhibition efficiencies. Taner et al. [12] studied 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 in answering 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. [13]. The development of theoretical scales of electrophilicity and nucleophilicity 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 [14] definition of global electrophilicity. 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 [15–17].

Dafali et al. [18] has studied the corrosion inhibition efficiency of some bipyrazolic compounds: (**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; and (**L6**) *N,N*-(bis((3-carboethoxy-5-methyl-1*H*-pyrazol-1-yl)methyl)cyclohexylamine of copper in 3 % 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 the effect of sea water 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 had 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 into the substituent effect on the inhibition efficiency of **L1**, **L2**, **L3**, **L4**, **L5**, and **L6** compounds (Scheme 1) using DFT-based reactivity indexes.

## Theoretical background

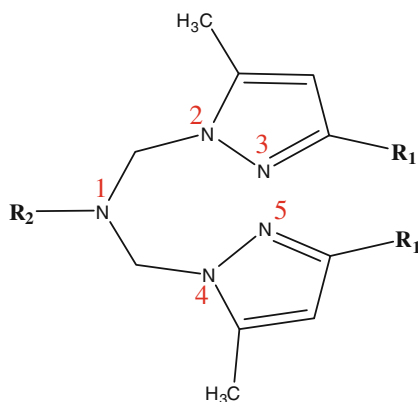
### Global quantities

Popular qualitative chemical concepts such as electronegativity [19, 20] ( $\chi$ ) and hardness [21] ( $\eta$ ) have been provided with rigorous definitions within the purview of conceptual density functional theory [22–24] (DFT). Electronegativity is the negative of chemical potential defined [25] as follows for an  $N$ -electron system with total energy  $E$  and external potential  $v(\vec{r})$ .

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

$\mu$  is the Lagrange multiplier associated with the normalization constraint of DFT [22, 26, 27].

**Scheme 1** Molecular structure of the bipyrazolic compounds studied



- L1:**  $R_1 = \text{CH}_3$ ;  $R_2 = \text{CH}_2\text{CH}_2\text{OH}$   
**L2:**  $R_1 = \text{CH}_3$ ;  $R_2 = \text{CH}_2\text{CH}=\text{CH}_2$   
**L3:**  $R_1 = \text{CH}_3$ ;  $R_2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$   
**L4:**  $R_1 = \text{CH}_3$ ;  $R_2 = \text{C}_6\text{H}_{11}$   
**L5:**  $R_1 = \text{CO}_2\text{CH}_3$ ;  $R_2 = \text{C}_6\text{H}_{11}$   
**L6:**  $R_1 = \text{CO}_2\text{C}_2\text{H}_5$ ;  $R_2 = \text{C-H}_{11}$

Hardness ( $\eta$ ) is defined [28] as the corresponding second derivative,

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

Using a finite difference method, working equations for the calculation of  $\chi$  and  $\eta$  may be given as [22]:

$$\chi = \frac{I + A}{2} \quad (3)$$

$$\eta = I - A \quad (4)$$

where  $I$  and  $A$  are the ionization potential and electron affinity, respectively. If  $\varepsilon_{\text{HOMO}}$  and  $\varepsilon_{\text{LUMO}}$  are the energies of the highest occupied and lowest unoccupied molecular orbitals, respectively, then the above equations can be rewritten, [29] using Koopmans' theorem [30], as

$$\chi = - \frac{\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}}}{2} \quad (5)$$

$$\eta = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \quad (6)$$

### 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  $v(r)$  [31].

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

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 [32].

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

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

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

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 [33, 34].

Domingo's definition of global and local nucleophilicity indexes

### The global nucleophilicity index $N$

According to Domingo et al. [15–17], the global nucleophilicity index,  $N$ , is defined by the following formula:

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

where  $\varepsilon_{\text{HOMO}(\text{Nu})}$  is associated to the HOMO energy within the Kohn–Sham scheme [35, 36] and  $\varepsilon_{\text{HOMO}(\text{TCE})}$  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.

#### The local nucleophilicity index $N_k$

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].

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

#### 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 [37]. The optimizations of equilibrium geometries of all reactants were performed using the Berny analytical gradient optimization method [38, 39]. The electronic populations as well as the Fukui indices and local nucleophilicities are computed using different populations analysis MPA (Mulliken population analysis) and NPA (natural population analysis) [40–43]. The cationic systems, needed in the calculation of nucleophilic Fukui indices, are taken in the same geometry as the neutral system.

## Results and discussion

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–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 1 and 2.

According to the nature of the  $R_1$  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

**Table 1** HOMO and LUMO energies, HOMO–LUMO gaps, electronic chemical potentials  $\mu$ , nucleophilicity indices  $Nu$ , hardness  $\eta$ , and the maximum electronic charge  $\Delta N_{\max}$  for compounds **L1–L6**

Compound	$R_2$	$R_1$	HOMO (a.u.)	LUMO (a.u.)	$\mu$ (a.u.)	$\eta$ (a.u.)	$\Delta N_{\max}$	$Nu$ (eV)	Gap (a.u.)	IE%
<b>L1</b>	CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>3</sub>	-0.2223	0.0191	-0.1016	0.241	0.42	3.31	-0.2414	99.5
<b>L2</b>	CH <sub>2</sub> CHCH <sub>2</sub>	CH <sub>3</sub>	-0.2208	0.0212	-0.0999	0.242	0.41	3.35	-0.2420	99
<b>L3</b>	C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	-0.2202	0.023	-0.0986	0.243	0.40	3.37	-0.2432	99.4
<b>L4</b>	C <sub>6</sub> H <sub>11</sub>	CH <sub>3</sub>	-0.2175	0.0270	-0.0953	0.244	0.38	3.44	-0.2445	98.9
<b>L5</b>	C <sub>6</sub> H <sub>11</sub>	CO <sub>2</sub> CH <sub>3</sub>	-0.2250	-0.0303	-0.1277	0.194	0.65	3.24	-0.1948	94.4
<b>L6</b>	C <sub>6</sub> H <sub>11</sub>	CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	-0.2252	-0.0290	-0.1271	0.196	0.64	3.23	-0.1964	94.6

<sup>a</sup> The HOMO energy,  $-0.34426$  a.u., of the reference system (TCE) has been calculated at the same computational level

<sup>b</sup> IE% =  $(1 - I/I_0) \cdot 100$  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  $\mu$ , nucleophilicity indices  $N_{i\mu}$ , hardness  $\eta$ , and the maximum electronic charge  $\Delta N_{\max}$  for compounds **L1–L6**

Compound	$R_2$	$R_1$	HOMO-1 (a.u.)	LUMO (a.u.)	$\mu$ (a.u.)	$\eta$ (a.u.)	$\Delta N_{\max}$	N (eV)	Gap (a.u)	IE%
<b>L1</b>	CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>3</sub>	-0.2247	0.0191	-0.1028	0.243	0.42	3.25	-0.2438	99.5
<b>L2</b>	CH <sub>2</sub> CHCH <sub>2</sub>	CH <sub>3</sub>	-0.2260	0.0212	-0.1024	0.247	0.41	3.21	-0.2472	99
<b>L3</b>	C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	-0.2244	0.0230	-0.1007	0.247	0.40	3.26	-0.2474	99.4
<b>L4</b>	C <sub>6</sub> H <sub>11</sub>	CH <sub>3</sub>	-0.2217	0.0270	-0.0973	0.248	0.39	3.33	-0.2487	98.9
<b>L5</b>	C <sub>6</sub> H <sub>11</sub>	CO <sub>2</sub> CH <sub>3</sub>	-0.2358	-0.0303	-0.1330	0.205	0.64	2.95	-0.2055	94.4
<b>L6</b>	C <sub>6</sub> H <sub>11</sub>	C0 <sub>2</sub> C <sub>3</sub> H <sub>5</sub>	-0.2362	-0.0290	-0.1326	0.207	0.63	2.93	-0.2073	94.6

copper corrosion [18]. The slight decrease in the inhibition efficiency observed between **L1**, **L2**, **L3**, **L4**, **L5**, and **L6** is due to an effect of  $R_1$ . It is worth noting that the experiment showed that the substitute fixed on the nitrogen of the amine does not have much effect on the inhibition efficiency.

The choice of a given molecular orbital (MO) to rationalize the chemical reactivity should be noted. The previous knowledge of the particular MO shape [15, 16] should certainly be necessary. 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 Fig. 1), it was concluded that the HOMO of these bipyrazolic compounds does not match the aromatic  $\pi$  system of the two pyrazole rings, but rather the other fragments of molecules. However, it was shown experimentally that the two nitrogen atoms in the cyclic rings and the

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

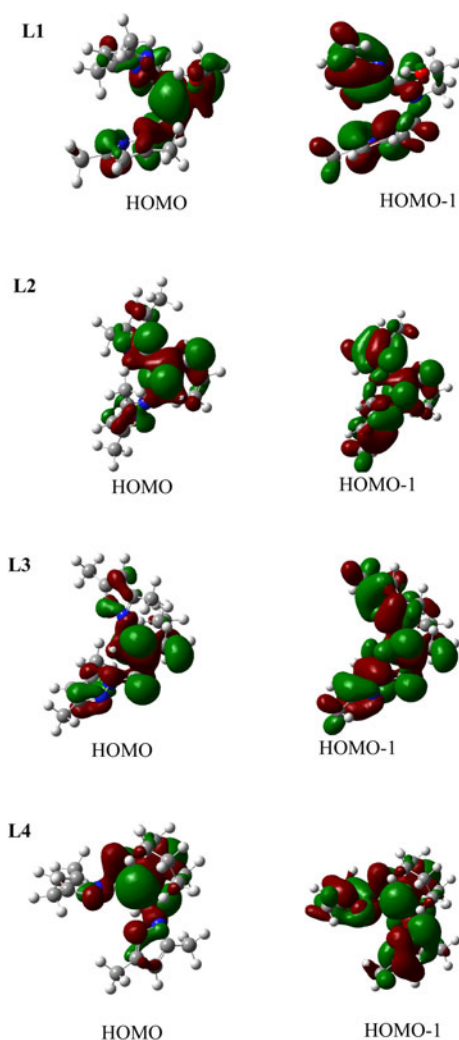
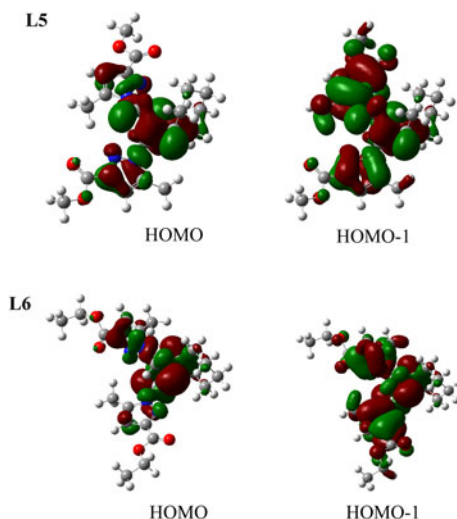


Fig. 1 continued



various substitutes are the major active centers of the adsorption. Indeed, the HOMO of these compounds does not contribute to an explanation of their efficiency inhibition, but the HOMO-1 can carry out 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 Fig. 1; 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.

By analyzing the HOMO-1–LUMO energy gap 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 electron-donating groups) are predicted to be better corrosion inhibitors of gaps of HOMO-1–LUMO (**L1**:  $-0.2438$ , **L2**:  $-0.2472$ , **L3**:  $-0.2474$ , **L4**:  $-0.2487$  a.u.) than the **L5–L6** compounds (substituted by electron-withdrawing 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 of these species are consistent with the calculated electronic chemical potentials,  $\mu$ , and the global nucleophilicity indexes showing that **L1**  $\mu = -0.1028$  a.u.;  $N = 3.01$  eV; **L2**  $\mu = -0.1024$  a.u.;  $N = 2.97$  eV, **L3**  $\mu = -0.1007$  a.u.;  $N = 3.01$  eV and **L4**  $\mu = -0.0973$  a.u.;  $N = 3.09$  eV are characterized by the highest chemical potential and global nucleophilicity compared to **L5**  $\mu = -0.1330$  a.u.;  $N = 2.70$  eV and **L6**  $\mu = -0.1326$  a.u.;  $N = 2.69$  eV.

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 center inhibitors requires information on the spatial

distribution of the electron density of these compounds [15, 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. The local nucleophilicity indexes,  $N_k$  are 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 indices. 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 transfer electrons from nitrogen to the copper surface.

### 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 Figs. 2, 3, 4, 5 and 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 becomes better when the system is characterized by high values of the electronic chemical potential, HOMO-1 energy, LUMO energy, nucleophilicity and low values of the HOMO-1–LUMO energy gap, in other words the efficiency of inhibition varies proportionally with  $E_{\text{HOMO-1}}$ ,  $E_{\text{LUMO}}$ ,  $N$ , and  $\mu$ ; however, it is inversely proportional to the  $E_{\text{HOMO-1}} - E_{\text{LUMO}}$  energy gap. On the other hand, we used multiple regressions (MLR) to obtain the best correlations between IE% and more than one parameter. The best correlation with experimental IE% ( $R^2 = 0.997$ ) is obtained using the three variables  $E_{\text{LUMO}}$ ,  $\mu$ , and the gap with a good statistical parameter (Fisher test,  $p$  value, Student's  $t$  test, the error SD). The equation of multiple linear regression (MLR) of this model is:

$$\text{IE}\% = 160 + 27,439 \text{ LUMO} - 27,160\mu + 13,850 \text{ gap}$$

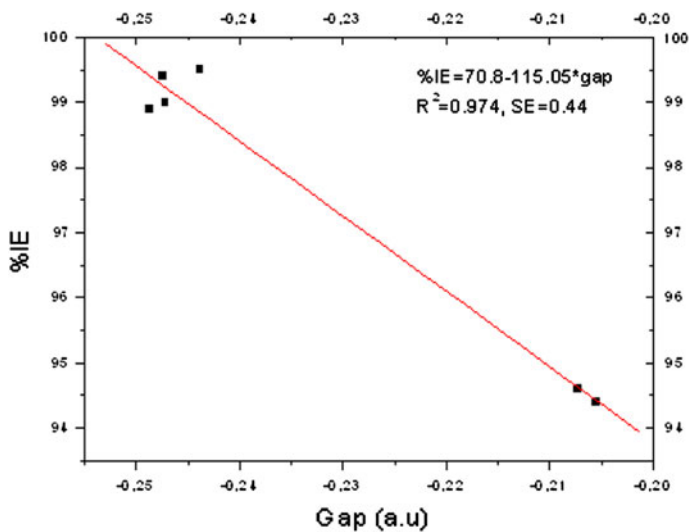
( $R^2 = 0.997$ ,  $\text{SD} = 0.20$ , Fisher test = 253.15,  $p$  value < 0.05,  $t$  test > 2)

### Conclusion

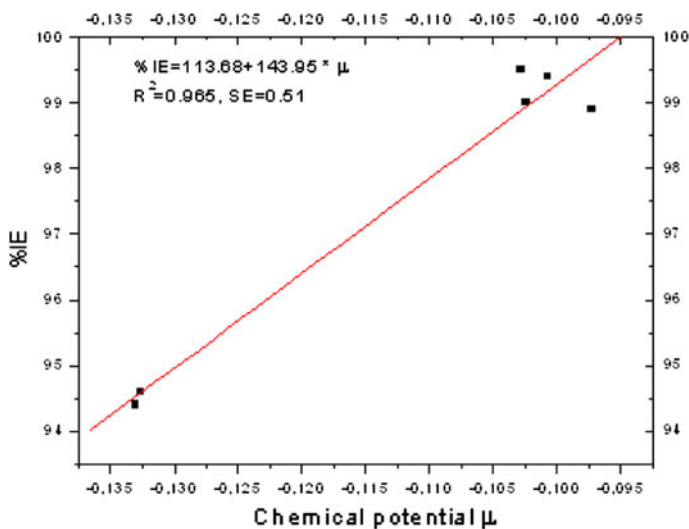
The tripod bipyrazoliques studied are effective for inhibiting corrosion of copper in a solution of 3 % NaCl. In comparing the percentages of inhibition efficiency (IE%) of the studied compounds with the theoretical results, we note that their inhibitory effects are closely related to  $E_{\text{HOMO-1}}$ ,  $E_{\text{HOMO-1}} - E_{\text{LUMO}}$  gap, nucleophilicity ( $N$ ) and the electronic chemical potential ( $\mu$ ). These parameters were calculated by

**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** systems and O for **L1**

Indexes compound	$N_1$		$N_2$		$N_3$		$N_4$		$N_5$		O	
	$f_k^-$	$N_k^-$	$f_k^-$	$N_k^-$	$f_k^-$	$N_k^-$	$f_k^-$	$N_k^-$	$f_k^-$	$N_k^-$	$f_k^-$	$N_k^-$
<b>L1</b>	0.1672	0.50	-0.0084	-0.03	0.0356	0.11	0.0053	0.02	0.0760	0.23	0.0429	0.13
<b>L2</b>	0.4317	1.28	0.0864	0.26	0.2790	0.83	0.0896	0.27	0.2743	0.81		
<b>L3</b>	0.1307	0.39	-0.0096	-0.03	0.1054	0.32	-0.0158	-0.05	0.0663	0.20		
<b>L4</b>	0.1336	0.41	-0.0121	-0.04	0.0987	0.30	-0.0043	-0.01	0.0749	0.23		
<b>L5</b>	0.2578	0.70	0.0029	0.01	-0.0170	-0.05	-0.0139	-0.04	0.0585	0.16		
<b>L6</b>	0.2536	0.68	0.0120	0.03	-0.0255	-0.07	-0.0194	-0.05	0.0601	0.16		

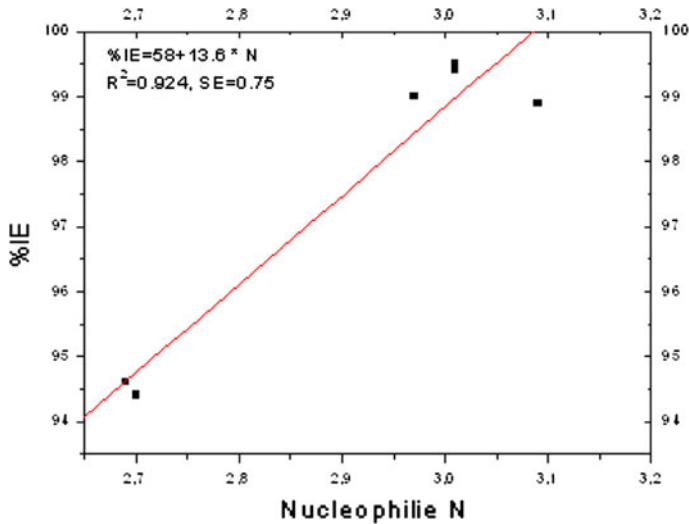


**Fig. 2** Correlation of LUMO energy with percent inhibition of **L1–L6**

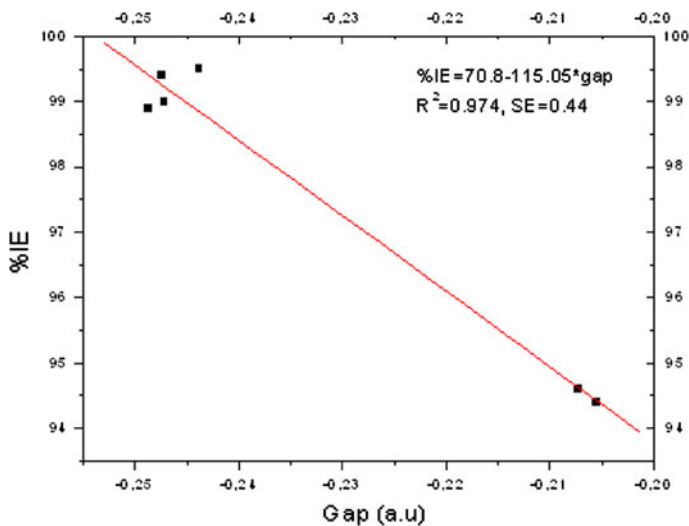


**Fig. 3** Correlation of chemical electronic potential  $\mu$  with percent inhibition of **L1–L6**

the DFT method. The IE% increases when  $E_{\text{HOMO-1}}$ ,  $N$  and  $\mu$  increase, and when the  $E_{\text{HOMO-1}} - E_{\text{LUMO}}$  gap decreases. Therefore, compounds **L1–L4** are better corrosion inhibitors (presence of donor groups on the pyrazole ring) than **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.

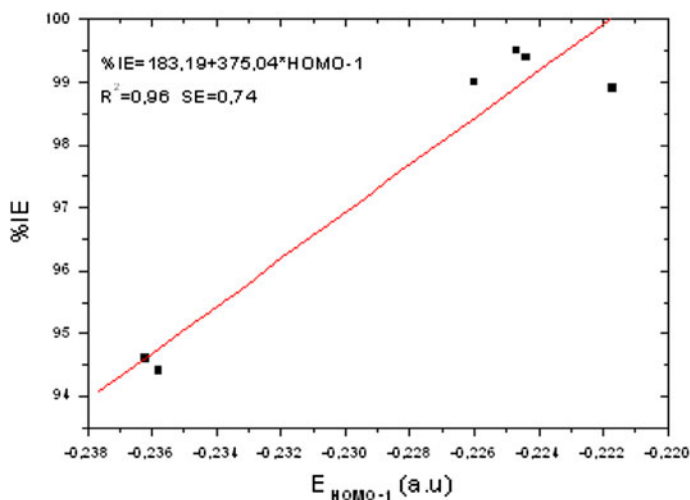


**Fig. 4** Correlation of nucleophilicity  $N$  gaps with percent inhibition of **L1-L6**



**Fig. 5** Correlation of  $E_{\text{HOMO}-1} - E_{\text{LUMO}}$  energy gaps with percent inhibition of **L1-L6**

The local indices nucleophilicity  $N_k$  of the series of bipyrazolic compounds were discussed in a simple but precise manner. 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



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

effect on the efficiency of inhibition, unlike the effect of the substituent on the pyrazole ring. This is in perfect agreement with the experiments.

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