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DFT study of new bipyrazole derivatives and their potential activity as corrosion inhibitors

Hengliang Wang · Xueye Wang · Hanlu Wang · Ling Wang · Aihong Liu

Abstract In the present work, a theoretical study of five bipyrazolic-type organic compounds, 4-{bis[(3,5-dimethyl-1*H*-pyrazolyl-1-yl)methyl]-amino}phenol (**1**), N1,N1-bis[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl}]-N4,N4-dimethyl-1,4-benzenediamine (**2**), N,N-bis[(3,5-di-methyl-1*H*-pyrazol-1-yl)methyl]aniline (**3**), 4-[bis(3,5-di-methyl pyrazol-1-yl-methyl)-amino]butan-1-ol (**4**) and ethyl4-[bis(3,5-dimethyl-1*H*-pyrazol-1-yl-methyl) amino-benzoate] (**5**), has been performed using density functional theory (DFT) at the B3LYP/6-31G(d) level in order to elucidate the different inhibition efficiencies and reactive sites of these compounds as corrosion inhibitors. The efficiencies of corrosion inhibitors and the global chemical reactivity relate to some parameters, such as EHOMO, ELUMO, gap energy (ΔE) and other parameters, including electronegativity (χ), global hardness (η) and the fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN). The calculated results are in agreement with the experimental data on the whole. In addition, the local reactivity has been analyzed through the Fukui function and condensed softness indices.

Keywords Bipyrazole · Corrosion inhibitors · Density functional theory (DFT) · Fukui function · Softness indices

Introduction

Corrosion of metal is a major industrial problem that has received a considerable amount of attention. The prevention of corrosion plays an important role in economics and safety. The use of inhibitors is one of the most practical methods to protect metals against corrosion, especially in acidic media [1]. Most efficient inhibitors are organic compounds containing electronegative functional groups and π-electrons in triple or conjugated double bonds. Heteroatoms like sulfur, phosphorus, nitrogen and oxygen as well as aromatic rings in their structure are the major adsorption centers.

Quantum chemical calculations have been widely used to study reaction mechanisms. They have also proved to be a very powerful tool for studying inhibition mechanisms [2]. The relationship between structural parameters, such as electronic properties of inhibitors, the frontier molecular orbital energy (E_{HOMO}, E_{LUMO}), the charge distribution of the inhibitors studied and their inhibition efficiencies were investigated in these studies.

The objective of this work is to present a theoretical study of the electronic and molecular structures of several newly synthesized bipyrazolic-type organic compounds, obtained through quantum chemistry calculations carried out with the Gaussian 03W program [3]. In addition, we attempt to find the correlation between the molecular structures of these compounds and their possible behavior as corrosion inhibitors. The molecules tested (Fig. 1) are: 4-{bis[(3,5-dimethyl-1*H*-pyrazolyl-1-yl)methyl]-amino}phenol (**1**), N1,N1-bis[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-N4,N4-dimethy-1,4-benzenediamine (**2**), N,N-bis[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]aniline (**3**), 4-[bis(3,5-dimethyl pyrazol-1-yl-methyl)-amino]butan-1-ol (**4**)

H. Wang · X. Wang (✉) · H. Wang · L. Wang · A. Liu
College of Chemistry, Xiangtan University,
Xiangtan 411105, People's Republic of China
e-mail: wxueye@xtu.edu.cn

Structure	Abbreviation
	1
	2
	3
	4
	5
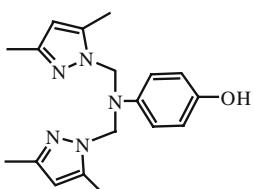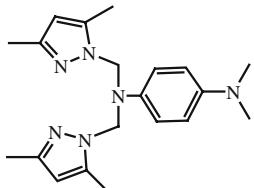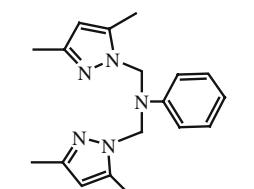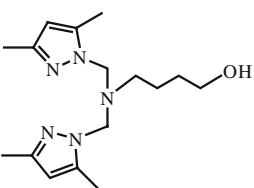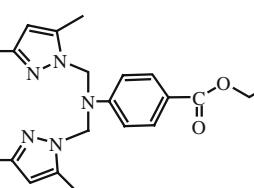
Fig. 1 Chemical formulas of the investigated compounds

and ethyl4-[bis (3,5-dimethyl-1*H*-pyrazol-1-yl-methyl) aminobenzoate] (**5**) [4–6].

Theory and computational details

Among quantum chemical methods for evaluation of corrosion inhibitors, density functional theory (DFT) has some merits [7]. B3LYP, a version of the DFT method that 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) [8], has been recognized especially for systems containing transition metal atoms [9, 10]. It has much less convergence problems than those commonly found for pure DFT methods. Thus, B3LYP was used in this paper to carry out quantum calculations. Then, full geometry optimizations of all inhibitors were carried out at the B3LYP/6-31G(d) level using the Gaussian 03W

program package. Many quantum chemical parameters that indicate structural characteristics of these organic inhibitors, such as E_{HOMO}, E_{LUMO}, energy gap, charge distribution and so on, were obtained.

DFT also provides a convenient theoretical framework for calculating global and local indices that describe the inherent reactivity of chemical species quantitatively. The electronegativity χ has been identified as the negative of the chemical potential μ, which is the Lagrange multiplier in the differential equation in DFT $\mu = -\chi = (\partial E/\partial N)_{v(\vec{r})}$ where E is the total electronic energy, N is the number of electrons [11], and $v\left(\vec{r}\right)$ is the external electrostatic potential that the electrons feel due to the nuclei. The global hardness is defined as $\eta = 1/2(\partial^2 E/\partial N^2)_{v(\vec{r})} = 1/2(\partial \mu/\partial N)_{v(\vec{r})}$ [12], while the global softness S is the inverse of the global hardness [13]. Both χ and η are global properties characterizing the molecules as a whole. The Fukui function $f\left(\vec{r}\right)$, as proposed by Parr and Yang [14], is defined as the partial derivative of the electron density $\rho\left(\vec{r}\right)$ with respect to the total number of electrons N of the system at the constant external potential $v\left(\vec{r}\right) : f\left(\vec{r}\right) = \left(\partial\rho\left(\vec{r}\right)\Big/\partial N\right)_{v(\vec{r})}$. The condensed Fukui function calculations are based on the finite difference approximation and partitioning of the electron density $\rho(r)$ between atoms in a molecular system. Yang and Mortier [15] proposed f_{k} calculations from atomic charges using equations: for reaction with the electrophiles

$$f_k^- = q_N - q_{N-1} \tag{1}$$

for reaction with the nucleophiles

$$f_k^+ = q_{N+1} - q_N \tag{2}$$

where q_N, q_{N+1} and q_{N-1} are the atomic charges of the systems with N, $N+1$ and $N-1$ electrons, respectively. The condensed Fukui function is local reactivity descriptor and can be used only for comparing reactive atomic centres within the same molecule.

Condensed softness indices allowing the comparison of reactivity between similar atoms of different molecules can be calculated easily starting from the relation between the Fukui function $f\left(\vec{r}\right)$ and the local softness $S\left(\vec{r}\right)$.

$$S\left(\vec{r}\right) = \left(\partial\rho\left(\vec{r}\right)\Big/\partial N\right)_{v(\vec{r})}(\partial N/\partial\mu)_{v(\vec{r})}$$
$$= f\left(\vec{r}\right)S \tag{3}$$

All calculations, including geometry optimizations for all structures were performed with the B3LYP exchange-correlation corrected functional [16, 17] with the 6-31G(d) basis set using the Gaussian 03W package. As shown by De Proft et al. [18], the B3LYP functional appears to be reliable for calculating $f(r)$ and f_{k} indices.

Results and discussion

The optimized structures for the five inhibitors (**1**, **2**, **3**, **4** and **5**) in their ground states are shown in Fig. 2.

Global reactivity

The frontier orbitals (highest occupied molecular orbital—HOMO) and (lowest unoccupied molecular orbital—LUMO) of a chemical species are very important in defining its reactivity. Fukui [19] first recognized this. A good correlation has been found between the speeds of

Fig. 2 Optimized structures of **1**, **2**, **3**, **4** and **5** calculated with the B3LYP/6-31G(d) model chemistry
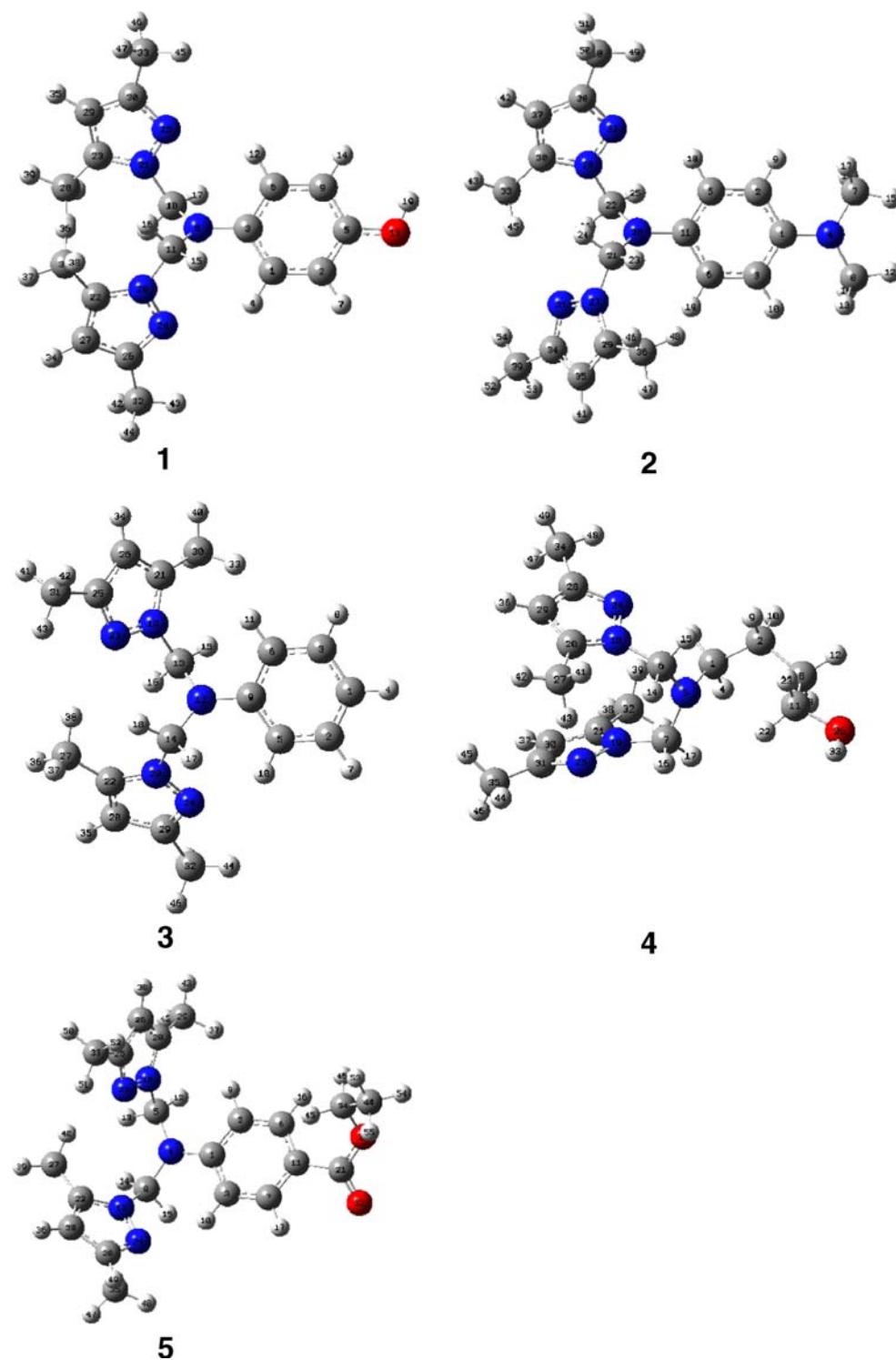
Table 1 HOMO and LUMO energies, LUMO–HOMO gap for **1**, **2**, **3**, **4** and **5**

Molecule	Total energy (a.u.)	HOMO (eV)	LUMO (eV)	ΔE
1	−1048.7155	−5.1541	0.1396	5.2937
2	−1107.4682	−4.7723	0.2223	4.9946
3	−973 .5030	−5.4934	0.1072	5.6006
4	−974.9021	−5.9734	0.7391	6.7125
5	−1240.6796	−5.7590	−0.7042	5.0548

corrosion and E_{HOMO} that is often associated with the electron-donating ability of the molecule. The literature shows that the adsorption of the inhibitor on the metal surface can occur on the basis of donor–acceptor inter-actions between the π-electrons of the heterocycle com-pound and the vacant d-orbitals of the metal surface atoms [20]. High values of E_{HOMO} have a tendency of the molecule 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 $\Delta E = E_{LUMO} - E_{HOMO}$ [21–23]. 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 it is that the molecule would accept electrons. Consequently, concerning the value of the energy of the gap $\Delta E = E_{LUMO} - E_{HOMO}$, larger values of the energy difference will provide low reactivity to a chemical species. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low [24, 25].

In Table 1, certain quantum-chemical parameters related to the molecular electronic structure are presented, such as: E_{HOMO}, E_{LUMO} and $\Delta E = E_{LUMO} - E_{HOMO}$. The values of E_{HOMO} show the relation **2**>**1**>**3**>**5**>**4** for this property. In addition, the values of the gap energy ΔE show the relation **4**>**3**>**1**>**5**>**2** for this property.

The results for the calculations of the ionization potential (I) and the electron affinity (A) by application of the Koopmans' theorem [21] are shown in Table 2. According

Table 2 Quantum-chemical descriptors for molecules **1**, **2**, **3**, **4** and **5**

Molecule	I	A	χ	η	ΔN
1	5.1541	−0.1396	2.5073	2.6469	0.8487
2	4.7723	−0.2223	2.2750	2.4973	0.9460
3	5.4934	−0.1072	2.6931	2.8003	0.7690
4	5.9734	−0.7391	2.6172	3.3563	0.6529
5	5.7590	0.7042	3.2316	2.5274	0.7455

Table 3 Fukui functions and local softness values for a nucleophilic and electrophilic for **1**

Number	Atom	f_k^+	f_k^-	S_k^+	S_k^-
1	C	0.0686	0.0335	0.0259	0.0127
2	C	0.0492	0.0218	0.0186	0.0082
3	C	−0.0058	0.0990	−0.0022	0.0374
5	C	0.0029	0.0325	0.0011	0.0123
6	C	0.0518	0.0348	0.0196	0.0132
9	C	0.0603	0.0242	0.0228	0.0091
8	N	−0.0048	0.0472	−0.0018	0.0178
20	N	−0.0241	−0.0018	−0.0091	−0.0007
21	N	−0.0054	−0.0017	−0.0021	−0.0006
24	N	0.0511	−0.0218	0.0193	−0.0082
25	N	0.0034	−0.0219	0.0013	−0.0083
13	O	0.0354	0.0830	0.0134	0.0314

to the Hartree–Fock theorem, the frontier orbital energies are given by: $-E_{HOMO} = I$, $-E_{LUMO} = A$. This theorem establishes a relation between the energies of the HOMO and the LUMO and the ionization potential and the electron affinity, respectively. Although no formal proof of this theorem exists within DFT, its validity is generally accepted. For χ and η, their operational and approximate definitions are $-\mu = (I + A)/2 = \chi$, $\eta = (I - A/2)$. Two systems, Fe and inhibitor, are brought together, electrons will flow from lower χ (inhibitor) to higher χ (Fe), until the chemical potentials become equal. As a first approximation, the fraction of electrons transferred [26], ΔN, will be given by

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2\left(\eta_{Fe} + \eta_{inh}\right)} \tag{4}$$

where Fe is the Lewis acid according to HSAB theory [27]. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [26].

Table 4 Fukui functions and local softness values for a nucleophilic and electrophilic for **2**

Number	Atom	f_k^+	f_k^-	S_k^+	S_k^-
1	C	0.0734	0.0157	0.0294	0.0063
2	C	0.0379	0.0293	0.0152	0.0118
3	C	0.0198	0.0341	0.0079	0.0136
5	C	0.0286	0.0215	0.0115	0.0086
6	C	0.0728	0.0163	0.0291	0.0065
11	C	0.0130	0.1157	0.0052	0.0463
20	N	−0.0136	0.0183	−0.0054	0.0073
27	N	−0.0002	−0.0147	−0.00001	−0.0059
28	N	0.0057	0.0037	0.0023	0.0015
31	N	0.0347	−0.0114	0.0139	−0.0046
32	N	−0.0096	−0.0182	−0.0039	−0.0073
4	N	−0.0280	0.0318	−0.0112	0.0127

Table 5 Fukui functions and local softness values for a nucleophilic and electrophilic for **3**

Number	Atom	f_k^+	f_k^-	S_k^+	S_k^-
1	C	−0.0045	0.0392	−0.0016	0.0140
2	C	0.0529	0.0112	0.0189	0.0040
3	C	0.0199	0.0101	0.0071	0.0036
5	C	0.0230	0.0380	0.0082	0.0136
6	C	0.0535	0.0433	0.0191	0.0155
9	C	0.0393	0.0479	0.0140	0.0171
12	N	−0.0115	0.0746	−0.0041	0.0266
19	N	−0.0029	−0.0259	−0.0010	−0.0092
20	N	0.0053	−0.0175	0.0019	−0.0062
23	N	0.0460	0.0005	0.0164	0.0002
24	N	−0.0025	−0.0097	−0.0009	−0.0035

In order to calculate the fraction of electrons transferred, a theoretical value for the electronegativity of bulk iron was used $\chi_{Fe} \approx 7eV$ [21], and a global hardness of $\eta_{Fe} \approx 0$, by assuming that for a metallic bulk $I=A$ [28] because they are softer than the neutral metallic atoms. From Table 2, it is possible to observe that molecule **2** has a lower value of global hardness. The fraction of transferred electrons is also the largest for molecule **2** and, in turn, is **1**, **3**, **5**, **4**. Therefore, according to a series of properties calculated for each molecule shown in Table 1 and Table 2, the reactivity order, that is, the inhibitive effectiveness order for the molecule is: **2>1>3>5>4**. The calculated results are in agreement with experiment [4–6].

Local selectivity

The local reactivity are analyzed by means of the condensed Fukui function, the condensed Fukui functions and condensed local softness indices allow us to distinguish each part of the molecule on the basis of its distinct chemical behavior due to the different substituent functional groups. Thus, the site for nucleophilic attack will be the place where the value of f^+ is a maximum. In turn, the site for electrophilic attack is controlled by the value of f^-. The values of the Fukui functions for a nucleophilic and electrophilic attack are given for the five inhibitors in Tables 3, 4, 5, 6, and 7, respectively (only for the nitrogen

Table 6 Fukui functions and local softness values for a nucleophilic and electrophilic for **4**

number	atom	f_k^+	f_k^-	S_k^+	S_k^-
5	N	0.0183	0.1192	0.0055	0.0355
18	N	0.0036	−0.0180	0.0011	−0.0054
19	N	0.0157	−0.0274	0.0047	−0.0082
24	N	0.0075	−0.0013	0.0022	−0.0004
25	N	0.0946	−0.0482	0.0282	−0.0144
26	O	0.0142	0.0382	0.0042	0.0114

Table 7 Fukui functions and local softness values for a nucleophilic and electrophilic for **5**

Number	Atom	f_k^+	f_k^-	S_k^+	S_k^-
1	C	0.1647	0.0252	0.0652	0.0100
2	C	−0.0057	0.0497	−0.0023	0.0197
3	C	−0.0293	0.0515	−0.0116	0.0204
6	C	0.0150	0.0266	0.0059	0.0105
7	C	0.0313	0.0237	0.0124	0.0094
11	C	0.0086	−0.0001	0.0034	−0.0001
4	N	−0.0135	0.0409	−0.0053	0.0162
18	N	−0.0136	−0.0096	−0.0054	−0.0038
19	N	−0.0002	0.0054	0.0041	0.0021
23	N	0.0285	−0.0201	0.0113	−0.0080
24	N	−0.0166	−0.0121	−0.0066	−0.0048
31	O	0.0600	0.0377	0.0237	0.0149
32	O	0.1607	0.0584	0.0636	0.0231

atom, oxygen atom and phenyl group). For nucleophilic attack, the most reactive site of the **1**, **3**, **3** molecules is on the carbon atoms of the phenyl ring, molecule **4** is on the N (25) atom pertaining to one of the pyrazole ring and, molecule **5** is on the C (1) atom of the phenyl ring and the O (32) atom of the acyl functional group. For electrophilic attack, the most reactive site of molecule **1** is on the C (3) atom of the benzene ring and the O (13) atom of the hydroxyl group, molecule **2** and **3** both on the phenyl ring, molecule **4** on the N (5) atom and molecule **5** on the C (2) and C (3) atoms of the phenyl ring and the O (32) atom of the acyl functional group.

The condensed local softness indices S_k^+ and S_k^- are related to the condensed Fukui functions through Eq. 3. In Table 8, in order to obtain a overall conception with regard to the values of the Fukui functions and local softness for each phenyl ring of **1**, **2**, **3** and **5**, their averaged values of six carbon atoms at the phenyl ring are adopted for comparision.

It can be observed that the order of the average values of Fukui functions f_k^+ for the carbon atoms of the phenyl ring for **1**, **2**, **3**, **5** is **2>1>5≈3**. In the same way, the order of the averaged local softness indices S_k^+ values is **2>1>5>3**. Thus, the phenyl ring of **2** will be more reactive than the phenyl ring of the other molecules in a nucleophilic reaction.

Table 8 Fukui functions and local softness average values for six carbon atoms of the phenyl ring

| Average	1	2	3	5
f_k^+	0.0378	0.0409	0.0307	0.0308
f_k^-	0.0410	0.0388	0.0316	0.0294
S_k^+	0.0143	0.0164	0.0110	0.0122
S_k^-	0.0155	0.0155	0.0113	0.0117
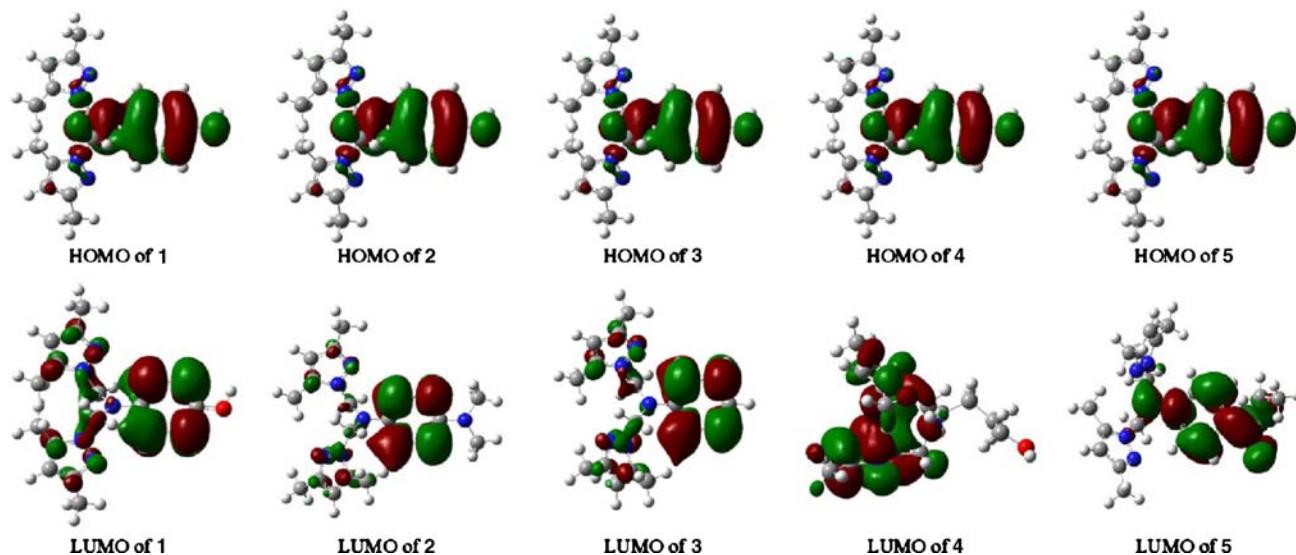
Fig. 3 Frontier molecular orbital diagrams of **1**, **2**, **3**, **4** and **5** by the B3LYP/6-31G(d) model chemistry

Figure 3 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecules under study. From these figures, it can be observed that the compounds **1**, **2**, **3** and **5** present a clear contribution of ρ-orbitals pertaining to the phenyl ring on the HOMO and LUMO. The exception is molecule **4**, in which the HOMO and LUMO are mainly located at the pyrazole ring.

Conclusions

In order to know the reactive behavior of five newly synthesized bipyrazolic-type organic compounds **1**, **2**, **3**, **4** and **5** as corrosion inhibitors, a theoretical study has been performed using the B3LYP functional with the 6-31G(d) basis set. By means of the calculation of the HOMO, the energy gap ΔE and the fraction of transferred electrons ΔN, the conclusion of the inhibitive effectiveness order for the molecule is: **2>1>3>5>4**, and this agrees well with experiment.

The values of the Fukui functions indicate the sites for nucleophilic and electrophilic attack. By means of the calculation of the Fukui functions, we reached the conclusion that the for the nucleophilic and electrophilic attack, reactive sites of **1**, **2**, **3** and **5** are located mainly in the phenyl rings, as well as in certain N or O atoms. The exception is **4**, which presents other reactive sites mainly located in atoms of nitrogen because of lacking the phenyl ring. In addition, the values of the Fukui functions and local softness for six carbon atoms of each phenyl ring of the **1**, **2**, **3** and **5** molecules are averaged in order to obtain a overall comparison about the reactivity for the phenyl rings, and the order of the Fukui functions f_k^+ is **2>1>5≈3**, the

local softness indices S_k^+ is **2>1>5>3**. Thus, the phenyl ring of **2** will be more reactive than the phenyl rings of the other molecules in a nucleophilic reaction.

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