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Quantum Chemical Studies on N-Donors Based-Pyrazole Compounds as Corrosion Inhibitors for Steel in Acidic Media

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In this study, some possible relationship between the experimental inhibition corrosion in acidic media and the theoretical energy calculations for four series of compounds containing pyrazoles: (A) the first series of compounds, comprises only one pyrazole ring, (B) the second series has two pyrazoles (bipyrazole), (C) the third one contains one pyrazole and one pyridine (pyridyl pyrazole) and (D) the last series concerns tripodal pyrazoles, has presented. These sets of compounds have been tested for their corrosion inhibition properties of steel in low concentration of hydrochloric acid medium. For these compounds, DFT method studies have been performed. They were based on (E_{HOMO}), (E_{LUMO}) and the difference (E_{LUMO}-E_{HOMO}). The correlation between these two parameters (theoretical and experimental) was shown to be in good agreement for some cases.

Key Words: Pyrazole, Bipyrazole, Pyridylpyrazole, Tripods, Corrosion inhibitors, Quantum chemical calculations.

INTRODUCTION

Pyrazole-based ligands form a variety of coordination complexes with a number of metals ions, providing varying coordination geometry and nuclearity[1]. The key feature of these heterocycles is their π-electron deficiency. Hence they behave as excellent π-acceptors which provide soft sites for metal coordination. On the other hand, the π-excessive five membered nitrogen heterocycle, pyrazole is a poorer π-acceptor. In fact, it is a better π-donor and hence acts as hard donor site. Recently, the systems based on nitrogen have known considerable interest in the designing of various

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pyrazole ligands and their properties[2-4]. The derivatives containing pyrazole appeared to be good corrosion inhibitors of steel in acidic medium[5-9]. These organic molecules can be adsorbed on the metal surface forming a connection between the electron pair and the nitrogen atoms or the electronic orbital π cloud reducing the corrosive attack of metal in acidic medium[10,11]. In addition, more recently, several corrosion inhibition semi-empirical studies have been realized with a view to establish a correlation between the experimental inhibition efficiency and the theoretical data[12-15]. The electronic properties of the inhibitors, the effect of energies E_{LUMO} and E_{HOMO} and the hydrophilic and hydrophobic nature of these organic compounds were brought back in these studies. In this study, a theoretical study of the electronic and energy properties E_{LUMO} and E_{HOMO} as well as the difference (E_{LUMO}-E_{HOMO}) of the constituents of four series of compounds containing pyrazole are reported. A comparison between the inhibiting efficiencies and theoretical calculations for each series of compounds will be presented.

METHOD OF CALCULATION

Theoretical calculations were carried out by using the Gaussian 03W software, version 6.0 on a PC (Pentium IV)[16]. The conformational analysis of the various geometries was performed with the help of the EMO program (Energy of Molecule) using the option SCAN. The minimization of the structures obtained was carried out using the EMO program (Champ de force MM2-Allinger) and finally we have used the DFT (DFT/B3LYP/6-31G* POP=NPA)[17-20].

RESULTS AND DISCUSSION

In order to obtain more information about a possible correlation between the corrosion inhibition efficiency of the ligands in acidic medium and the quantum theoretical chemical calculation parameters, four different series of compounds containing pyrazole (A, B, C and D) were selected (Fig. 1). These compounds were synthesized according to the literature methods. The first series (A) contains L1 and L2[21]; the second series (B) has two pyrazole groups (bipyrazole)[22]; the third series (C) possesses one pyrazole and one pyridine (pyridylpyrazole)[23,24] and the last series (D) contains tripodal compounds[25]. The theoretical quantum calculations were performed taking compounds shown in Fig. 2 as references. Their corrosion inhibition efficiency (E (%)) of steel in 1 M HCl medium has been performed in our laboratory using 10^{-3} M as concentration of the ligand inhibitor, by two different methods: gravimetric and electrochemical. The experimental results are given on Table-1. When comparing the [E (%)] for the first series (A), the ligand L2 (having hydroxyl group) shows a better inhibition efficiency than the ligand L1 (having ester group), this may be due to the electron deficiency caused by the presence of the ester group, thus, we may conclude that L2 > L1[26] (Table-1). Concerning the series (B), the classification obtained is L5 > L6 > L3 > L4. The same interpretation about the presence of the ester in the ligand L4, which decreases the electronic density of the entire compound, may be valuable. On the other hand, the presence of the hydroxyl group at position α or β of the pyrazole ring causes a drastic changes *e.g.,* L5 [E (%) = 93] and L6 [E (%) = 81][27]. This may be due to the steric effect caused by the hydroxyl chain group. As regards to the third series (C), the obtained results are comparable to the experimental ones for the inhibition corrosion of steel in 1 M HCl medium (with ligand concentration = 10^{-3} M).

TABLE-1

CORROSION INHIBITING EFFICIENCY [E (%)] OF STEEL IN 1 M HCl MEDIUM AS OBTAINED FOR THE DIFFERENT INHIBITORS WITH A CONCENTRATION OF 10^{-3} M USING THE GRAVIMETRIC AND ELECTROCHEMISTRY METHODS

Ligand	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L12
Gravimetry E (%)	38	74	79	74	93	81	89	94	87	89	95	91
Electrochemistry E (%)	32	68	76	-	89	78	91	92	81	78	-	-

The classification of the [E (%)] of these compounds is L8 > L7 > L9 = L10. The presence of the hydroxyl group at position β of the pyridylpyrazole (L8) leads to a better inhibition efficiency[28] than the other substituents (Table-1). For the last series (D) which contains tripodal compounds, unpublished results show that the classification is L11 > L12.

One pyrazole (A): The discussions concerning the results obtained using the theoretical methods applied to these structures are based on the value of the energy of LUMO (E_{LUMO}) which indicates the relative stability of the different possible geometries, (*i.e.* minimum energy → maximum stability → structure could be easily rearranged)[29-33]. Interestingly, as regards the gaps [$\Delta E(a.u.) = E_{LUMO} - E_{HOMO}$] and $\Delta(\Delta E) = (\Delta E_{ref.} - \Delta E)$, these parameters allow an information on the efficiency of the inhibiting capacity [*i.e.* low gap ΔE(a.u.) → high capacity]. The dipole moment μ represents interesting information, which can in certain cases confirm the first two approaches (μ increases → inhibiting effectiveness increases too)[34-36]. In other cases, when compared to the literature, the present study reveals certain irregularities of correlation between the dipole moment and the inhibiting capacity[37-39].

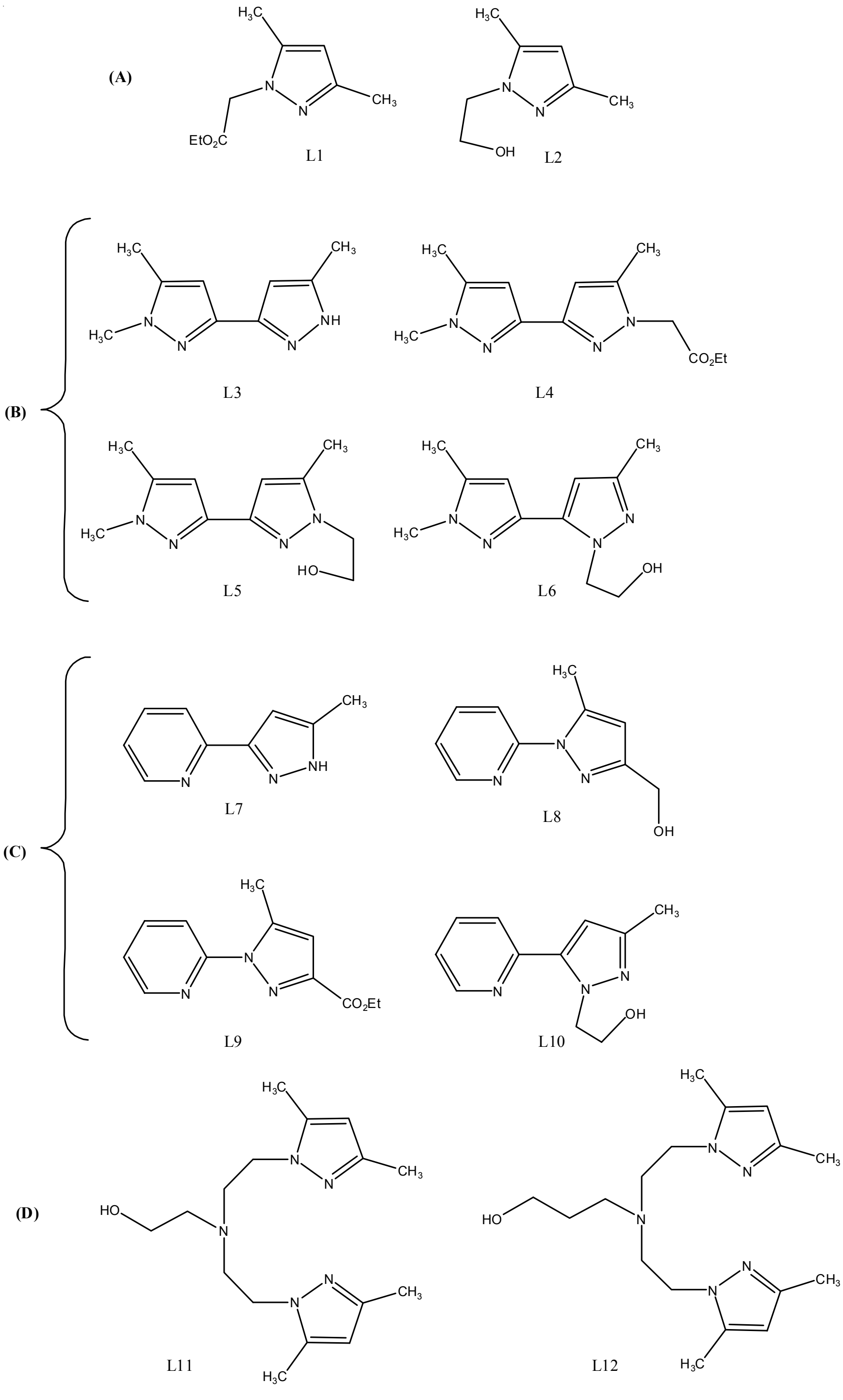
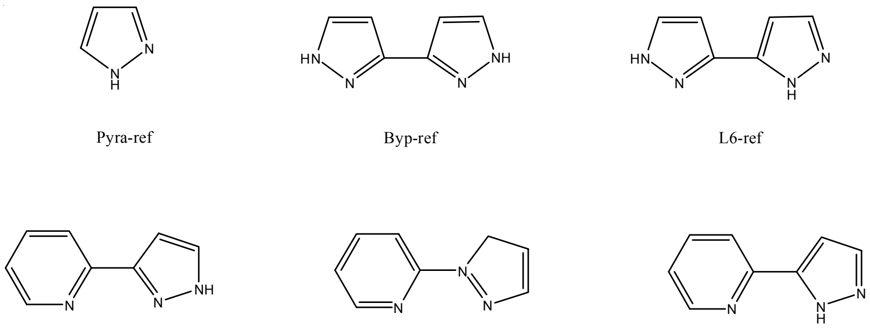


Fig. 1. List of ligands used as corrosion inhibitors of steel in 1 M HCl medium

On the basis of results obtained at the time of present work, the classification may be L2 > L1 (Table-2): Compared to Pyra-ref (Fig. 2). Compared to the effect of grafting of groupings on Pyra-ref and ΔE(Pyra-ref) > ΔE(L1) > ΔE(L2). For this series, it is concluded that a satisfactory correlation between the experimental studies and the theoretical calculations.

TABLE-2
THEORETICAL CALCULATION FOR THE SERIES (A)

	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	ΔE (a.u.)	μ (D)	Δ(ΔE) (a.u.)
Pyra-ref	-0.24724	0.01398	0.26122	2.4676	–
L1	-0.23029	-0.01204	0.21825	3.6667	0.04297
L2	-0.11035	0.09177	0.20212	3.4014	0.05910



Pyra-ref Byp-ref L6-ref

L7- ref L9-ref L10- ref

Fig. 2. References products

Two pyrazoles (bipyrazole) (B): From Table-3, it is concluded that the classification of the ligands from the lowest ΔE(a.u.) (good efficiency) to the highest is L4 > L6 > L5 > L3. The comparison of the experimental and the theoretical results shows that the correlation in this case is not quite satisfactory. Indeed, the compound L5 with a hydroxyl group should be more efficient than the compound L4.

TABLE-3
THEORETICAL CALCULATION OF SERIES (B)

	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	ΔE (a.u.)	μ (D)	Δ(ΔE) (a.u.)
Byp-ref	-0.21883	-0.00243	0.21640	0.0009	–
L3	-0.20425	0.00631	0.21056	0.4760	0.00584
L4	-0.20356	-0.01074	0.19282	2.5076	0.02358
L5	-0.21113	-0.00588	0.20525	3.0433	0.01115
L6-ref	-0.21903	-0.01968	0.19935	4.9509	–
L6	-0.20956	-0.01136	0.19820	4.3932	0.00115

One pyrazole and one pyridine (pyridylpyrazole) (C): The theoretical calculations for the third series which contains one pyrazole and one pyridine (Table-4) show that the classification of the ligands in the same series is as follow: L9 > L8 > L10 > L7. The examination of the experimental and theoretical results leads to a better correlation for compound L8 than the rest of the series. This is not the case for the ligand L7 which exhibit a poorer correlation.

TABLE-4
THEORETICAL CALCULATION OF SERIES (C)

	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	ΔE (a.u.)	μ (D)	Δ(ΔE) (a.u.)
L7-ref	-0.16140	0.04838	0.20978	1.7088	–
L7	-0.22421	-0.02881	0.19540	1.8955	0.01438
L10-ref	-0.22899	-0.04913	0.17986	3.8760	–
L10	-0.23421	-0.05408	0.18013	6.4111	0.00027
L8-ref	-0.24103	-0.03779	0.20324	4.1149	–
L8	-0.24374	-0.05500	0.18874	2.7461	0.01450
L9-ref	-0.17140	0.03784	0.20924	3.6487	–
L9	-0.23418	-0.04035	0.19383	3.8282	0.01541

Two pyrazoles and one amine (D):

TABLE-5
THEORETICAL CALCULATIONS FOR THE SERIES (D)

	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	ΔE (a.u.)	μ (D)
L11	-0.21445	0.01844	0.23289	1.5178
L12	-0.20378	0.02072	0.22450	4.1200

As can be observed from Table-5, the ligand L12 is better than the ligand L11 (L12 > L11). In addition, the correlation between the experimental results using the gravimetric method and the theoretical predictions are not in good agreement.

Conclusion

As a conclusion, the correlation between experimental and predicted results has been more limited than would have been desirable for almost the entire series under investigation. Thus, a general rule was not possible to establish according to the present results. Nevertheless, a quite satisfactory correlation was obtained for the ligand L8 belonging to the series (C). It is worthnoting that this type of molecule have been shown to exhibit antitumor properties which encourages us to project a similar study in order to correlate their biological activity with the theoretical calculations.

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