DFT-based QSAR Study of Substituted Pyridine-Pyrazole Derivatives as Corrosion Inhibitors in Molar Hydrochloric Acid

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Quantum chemical calculations, based on DFT methods at B3LYP/6-31G** level of theory, were performed, by means of the G03 set of programs, on four pyridine-pyrazole compounds. The objective of this work was to attempt to find relationships between the intrinsic electronic properties and inhibiting efficiencies of two pyridine-pyrazole derivatives, denoted H-PP and Br-PP, which have been previously studied experimentally as mild steel corrosion inhibitors in acidic medium. Based on these results, the Quantitative Structure–Activity Relationships (QSAR) studies allowed us to calculate the inhibitive efficiencies for the former and for two other pyridine-pyrazole derivatives, Cl-PP and Me-PP, of which the experimental study, was not yet made. The structural electronic properties of the whole pyridine-pyrazole molecules were investigated by means of number of global and local theoretical reactivity descriptors. The results showed that the electronic effect of the substituent at the meta of the pyridine ring markedly influenced the performance of the studied inhibitors. The QSAR's quadratic model results, representing the best fitting, showed that the Cl-PP and Me-PP will probably have the same corrosion inhibitory performance as Br-PP and H-PP, respectively especially at higher concentrations.

Keywords: DFT; Pyridine-pyrazole; Corrosion inhibition; PCM; QSAR.

1. INTRODUCTION

The corrosion is a degradation of material's properties, due to interfacial interactions with elements that recur within their environments, which generate irreversible damages and high material costs [1,2]. In order to prevent the damages caused by corrosion, the use of organic inhibitors has been found to be very effective [3-19]. The organic inhibitors interact with the metal surface by donating electrons to the vacant or partially filled *d* orbital of the metal, thereby the efficiency of these compounds depends on the functional groups present within their molecular structures such as heteroatoms (e.g., N, O, S and P), aromatic rings and conjugate π double or triple bonds. Thus, the effectiveness of corrosion inhibitors is highly linked to their structural and electronic properties. Therefore, the use of theoretical study to correlate the electronic descriptors with the corrosion inhibition efficiency has been widely used in order to explain the experimental results, and also to elucidate the mechanism of corrosion inhibition process [20-22]. The theoretical results can also be used to look for compounds with desired properties using Quantitative Structure Activity Relationships (QSAR) methods [23]. The ultimate goal is to be able to predict the corrosion inhibitive efficiency of any number of compounds, with similar structures, including those not yet experimentally studied employing quantum chemical approaches.

The aim of this work is to investigate, using Density Functional Theory (DFT), the electronic structure properties of four pyridine-pyrazole derivatives, shown in Table 1, as corrosion inhibitors for mild steel in acidic medium. The theoretical results are then used in the QSAR study for the development of nonlinear and quadratic equations to calculate corrosion inhibition efficiencies of the whole inhibitors, and especially to predict those of Cl-PP and Me-PP.

Inhibitor Formula	Name	Abbreviation
$Br \xrightarrow{H} N \xrightarrow{H_3C} N \xrightarrow{N} CH_3$	5-bromo-N-[(3,5-dimethyl-1H-pyrazol-1-yl) methyl] pyridin-2-amine	Br-PP
$CI \longrightarrow H$ H_3C N N CH_3	5-chloro-N-[(3,5-dimethyl-1H-pyrazol-1-yl) methyl] pyridin-2-amine	CI-PP
$ \begin{array}{c} & & H & H_3C \\ \hline & & & N & \\ & & & N & \\ & & & N & \\ & & & CH_3 \end{array} $	N-[(3,5-dimethyl-1H-pyrazol-1-yl)methyl] pyridin-2- amine	H-PP

Table 1. Molecular structures, names and abbreviations of the studied pyridine-pyrazole molecules



5-methyl-N-[(3,5-dimethyl-1H-pyrazol-1-yl) methyl] **Me-PP** pyridin-2-amine

2. COMPUTATIONAL DETAILS

All quantum chemical study was carried out using the Density Functional Theory (DFT) with hybrid functional B3LYP, based on Becke's three-parameter functional including Hartree–Fock exchange contribution with a nonlocal correction for the exchange potential proposed by Becke [24,25] together with the nonlocal correction for the correlation energy provided by Lee et al. [26]. Since electrochemical corrosion takes place in liquid phase, and for a better approach of the experimental results, we used the Self-Consistent Reaction Field (SCRF) theory [25], with Tomasi's Polarized Continuum Model (PCM) [27], to include the effect of solvent in the computations. This approach models the solvent as a continuum of uniform dielectric constant (ϵ) and defines the cavity where the solute is placed as a uniform series of interlocking atomic spheres.

The quantum chemical investigations were used to look for good theoretical parameters to be correlated with the inhibitive performance of the studied pyridine-pyrazole derivatives. To do so, some of molecular properties, describing the global reactivity such as: the energy of the Highest Occupied Molecular Orbital (E_{HOMO}), the energy of the Lowest Unoccupied Molecular Orbital (E_{LUMO}), the energy gap ($\Delta E = E_{LUMO}$ -E_{HOMO}), the electrical dipole moment (μ), the Ionization Potential (IP), the Electron Affinity (EA), the electronegativity (χ), the global hardness (η), and the fraction of transferred electrons (ΔN) were calculated. Other parameters describing the local selectivity of the studied molecules such as the local natural populations and the Fukui functions were also considered. In order to estimate some of the previous descriptors, the Koopmans' theorem was used [28] to relate the HOMO and LUMO energies to the IP and EA, respectively:

$$IP = -E_{HOMO} \tag{1}$$

$$EA = -E_{LUMO} \tag{2}$$

Then the electronegativity and the global hardness were evaluated, based on the finite difference approximation, as linear combinations of the calculated *IP* and *EA* [28]:

$$\chi = \frac{IP + EA}{2} \tag{3}$$

$$\eta = \frac{IP - EA}{2} \tag{4}$$

The fraction of transferred electrons ΔN was calculated according to Pearson theory [29]. This parameter evaluates the electronic flow in a reaction of two systems with different electronegativities, in particular case; a metallic surface (Fe) and an inhibitor molecule. ΔN is given as follows:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})}$$
(5)

where χ_{Fe} and χ_{inh} denote the absolute electronegativity of an iron atom (Fe) and the inhibitor molecule, respectively; η_{Fe} and η_{inh} denote the absolute hardness of Fe atom and the inhibitor molecule, respectively. In order to apply the eq. 5 in the present study, a theoretical value for the electronegativity of bulk iron was used $\chi_{Fe} = 7$ eV and a global hardness of $\eta_{Fe} = 0$, by assuming that for a metallic bulk IP = EA because they are softer than the neutral metallic atoms [29].

3. RESULTS AND DISCUSSION

3.1. Molecular geometries

The quantum chemical calculations are performed on an Intel (R) core (TM)₂ Quad CPU (2.4 GHz and 8 GB RAM) computer using standard Gaussian-03 software package [30]. The geometries of the pyridine-pyrazole derivatives considered in this work are fully optimized, without any symmetry constraint at DFT level of theory using a B3LYP functional together with 6-31G(d,p) basis set in gaseous phase. Besides, for a better approach of the experimental parameters, the geometries are re-optimized in aqueous phase at the same level of theory using PCM model. The final optimized geometries are given in Fig. 1 and the geometrical parameters values are presented in Table 2.

Angle	Phase	Br-PP	Cl-PP	H-PP	Me-PP
$[N_5, C_6, N_7]$	G	113.6	113.6	113.8	113.9
	А	114.2	114.2	114.4	114.5
$[C_6, N_7, C_8]$	G	122.3	122.4	122.4	122.1
	А	123.3	123.2	123.0	122.6
$[N_5, C_6, N_7, C_8]$	G	83.7	83.5	83.5	82.7
	А	79.5	79.5	79.8	78.4
$[N_1, N_5, C_6, N_7]$	G	64.4	64.3	65.2	64.9
	А	64.8	64.5	65.4	65.1
$[C_6, N_7, C_8, N_9]$	G	17.2	17.3	17.1	17.5
	А	15.0	15.2	16.3	17.7

Table 2. Pertinent valence and dihedral angles, in degree, of the studied inhibitors calculated at B3LYP/6-31G(d,p) in gas, *G* and aqueous, *A* phases

The analysis of Table 2 reveals that the geometries of the studied inhibitors are almost the same. The dihedral angles investigation show that the pyridine and the pyrazole rings are circa perpendicular to each other in all four compounds and approximately equal to $\sim 83^\circ$ in gas phase.

The structural analysis also shows that C11-Cl16 and C11-Br16 bonds are the longest among all the other bond lengths, ~1,76 Å and 1.91 Å, respectively. The large polarization of these bonds may allow better and easier adsorption onto the mild steel surface throughout the chlorine and the bromine

atoms and accordingly good inhibiting efficiency. It is to be noted that the computed structural parameters in solution show that the solvent effect on the structural parameters is nearly insignificant.



Figure 1. Optimized molecular structures and bond lengths of the studied inhibitors calculated in gas (black) and aqueous (red) phases at B3LYP/6-31G(d,p) level

3.2. Global molecular reactivity

The corrosion inhibitive process of organic molecules is defined as reaction involving the transfer of electrons between the inhibitor and the material surface. Hence, it can be explained according to Fukui's frontier molecular orbital theory, by the interaction between the HOMO and

LUMO of the reacting species [31]. The calculated energies of the frontier orbitals and other parameters derived from these orbitals as well as the corresponding experimental inhibiting efficiencies of Br-PP and H-PP [9] are collected in Table 3.

Table 3. Quantum chemical descriptors of the studied inhibitors at B3LYP/6-31G(d,p) in gas, G and aqueous, A phases and the inhibition efficiencies IE_{exp} as given in [9].

Inhibitor	Phase	E _{HOMO} eV	E _{LUMO} eV	ΔE eV	μ D	IP eV	EA eV	χ eV	η eV	ΔN	IE _{exp} %*
Br-PP	G	-5.878	-0.871	5.007	0.695	5.878	0.871	3.374	2.503	0.724	87
	А	-5.905	-0.871	5.034	1.331	5.905	0.871	3.388	2.517	0.717	
Cl-PP	G	-5.905	-0.898	5.007	1.792	5.905	0.898	3.401	2.503	0.719	-
	А	-5.932	-0.871	5.061	2.153	5.932	0.871	3.401	2.531	0.711	
H-PP	G	-5.769	-0.490	5.279	1.338	5.769	0.490	3.129	2.640	0.733	83
	А	-5.850	-0.544	5.306	1.663	5.850	0.544	3.184	2.640	0.723	
Me-PP	G	-5.633	-0.463	5.170	0.807	5.633	0.463	3.048	2.585	0.764	-
	А	-5.714	-0.544	5.170	1.792	5.714	0.544	3.129	2.585	0.749	

* Inhibiting efficiency determined at 10^{-3} M as reported in [9]

As E_{HOMO} is often associated with the electron donating ability of a molecule, high value of E_{HOMO} is likely to indicate the tendency of the molecule to donate electrons to an appropriate acceptor with lower energy empty molecular orbital. The calculated values of E_{HOMO} of the studied inhibitors in gas as well as in aqueous phases are presented in Table 3. The presence of the methyl group in Me-PP, as electron releasing group through the inductif (+I) effect at the meta of the pyridine ring, should increases the electron density on the aromatic ring, enhancing its nucleophilicity [32]. On the other hand, the (-I) withdrawing effect of chlorine and bromine atoms in Cl-PP and Br-PP, respectively, creates density deficiency on the pyridine ring, which will probably decrease their nucleophilicities. These assumptions explain the trend of the computed values of the E_{HOMO} of the studied inhibitors. Indeed, the Me-PP displays the highest value when Cl-PP and Br-PP have both the lowest values in comparison with H-PP, which indicates that Me-PP is more likely to undergo nucleophilic attack more than the three other studied inhibitors, especially Cl-PP and Br-PP. The order of decreasing HOMO energy of the undertaken inhibitors is as follows:

 E_{HOMO} (Me-PP) > E_{HOMO} (H-PP) > E_{HOMO} (Br-PP) > E_{HOMO} (Cl-PP)

Likewise, the E_{LUMO} is associated with the electron accepting ability of the molecule, consequently, the low value of E_{LUMO} the high tendency to accept electrons from suitable electron donors. The values of the E_{LUMO} presented in Table 3 show that Cl-PP and Br-PP have the lowest E_{LUMO} when compared to H-PP and Me-PP which indicate better capability of Cl-PP and Br-PP to accept electrons from the mild steel surface. This can also be explained by the electron deficiency on the pyridine ring resulting of the withdrawing effect of Cl and Br atoms. The decreasing E_{LUMO} can be ranked as follows:

 E_{LUMO} (Cl-PP) $< E_{LUMO}$ (Br-PP) $< E_{LUMO}$ (H-PP) $< E_{LUMO}$ (Me-PP)

The energy gap, ΔE between the HOMO and LUMO orbitals reflects the static chemical reactivity of the studied molecules. The obtained values of ΔE indicate that the substitution of the hydrogen atom in H-PP by methyl group (Me-PP) or by Cl and Br (Cl-PP and Br-PP, respectively) decreases the value of the energy gap. However, the values of Cl-PP and Br-PP (~ 5,007eV) are much lower than the one of Me-PP (5,170eV) indicating that the (-I) effect of the chlorine and bromine in the meta of the pyridine ring have probably greater influence on the reactivity of the studied inhibitors than the (+I) electronic effect of the methyl group in the same position. Therefore, the adsorption of Cl-PP and Br-PP onto the mild steel surface through the back donating mechanism will probably be stronger than the adsorption of Me-PP and H-PP, respectively. The decreasing energy gap is as follows:

$\Delta E (\text{Br-PP}) \approx \Delta E (\text{Cl-PP}) \leq \Delta E (\text{Me-PP}) \leq \Delta E (\text{H-PP})$

The dipole moment μ is a measure of the polarity of a covalent bond, which is related to the distribution of electrons in a molecule. However its relation to the efficiency of corrosion inhibitors is not yet well established and there is no agreement in the literature on the way of interpreting the trend of the dipole moment values in a set of corrosion inhibitors [20,33]. In fact, the computed values of the dipole moment do not allow any kind of interpretation with regards to the literature. From the computed results in aqueous phase (Table 3), we realize that the stabilization effect of the solvent is mainly noticed in the increase of the dipole moment μ values in solution, which is probably a result of the polarization of the inhibitor molecules (solutes) by the solvent, leading to an increase in the charge separation in the molecules [34].

The global hardness η is a very important parameter that describes the molecular reactivity. It is well established that hard molecules (atoms or ions) are more resistant to eventual deformation or polarization of the electronic cloud caused by a relatively small perturbation of molecular reactions [20-22]. Hence, inhibitors with the lowest values of global hardness are expected to be good corrosion inhibitors. The global hardness results presented in Table 3 show that Cl-PP and Br-PP have the lowest value of η (2.503eV), followed by Me-PP (2.585eV) when H-PP presents the highest value of η (2.640eV). These results corroborate the previous predictions, derived from gap of energy, of the high reactivity of Cl-PP and Br-PP in comparison to Me-PP and H-PP, respectively. The increasing global hardness for the studied inhibitors is as follows:

η (Br-PP) $\approx \eta$ (Cl-PP) $< \eta$ (Me-PP) $< \eta$ (H-PP)

According to Lukovits's study [35], the fraction of transferred electrons describes the trend of electrons donation within a set of inhibitor. Generally, in the case of ΔN less than 3.6, the inhibition efficiency increases with the increase in electron-donating ability to the metal surface. The obtained values of ΔN reported in Table 3 are all below 3.6 and show that Me-PP presents the higher value of ΔN , which implies good disposition of this inhibitor to donate electrons to the mild steel surface, especially, when compared to Cl-PP, probably as a result of the high withdrawing effect of the chlorine atom on the electron density of the pyridine ring in Cl-PP, which agree well with the above results of HOMO and LUMO energies tendency. The transferred electrons increase as follows:

 ΔN (Cl-PP) $\leq \Delta N$ (Br-PP) $\leq \Delta N$ (H-PP) $\leq \Delta N$ (Me-PP)

It is to be concluded from the evolution of the considered global descriptors that E_{LUMO} , ΔE and η follow the tendency of experimental inhibiting efficiencies of the studied molecules. In an opposite way, neither E_{HOMO} , μ nor ΔN do not constitute good index to describe the undertaken list of inhibitors.

Meanwhile, the frontier orbitals electrons density distributions are of great importance in describing the adsorption preference of the inhibitors. The calculated HOMO and LUMO electron density distributions of the studied inhibitors are presented in Fig. 2. The results show that the electron densities of the HOMO orbitals are mostly localized on the pyridine ring, which will probably confer to the inhibitors a strong adsorption onto the mild steel surface throughout this site. Also, the HOMO orbitals are partially localized on the pyrazole ring indicating that it should be a potential adsorption site onto the mild steel surface as well but with less importance when compared to the pyridine ring. However, the LUMO is almost completely localized on the pyridine ring. These distributions justify the impact of substitution especially on the pyridine ring which is probably most responsible site of the adsorption process of the undertaken pyridine-pyrazole derivatives.

3.3. Local molecular reactivity

Besides the global reactivity indicators, the analysis of atoms selectivity within inhibitors is very useful in indicating the reactive sites towards electrophilic and nucleophilic attacks. In the case of an electron-transfer for reaction control, the selectivity descriptors of choice are the condensed Fukui functions on atoms [36]. These descriptors inform about the veritable sites in a molecule on which nucleophilic, electrophilic or radical attacks are most likely possible.

In order to compute the condensed Fukui functions of a system of N electrons, we perform a single point calculation of the anionic (N+1) and the cationic (N-1) species by using the neutral optimized geometry, at the same level of theory. The condensed Fukui functions are then computed using the finite-difference approximation as follow:

$f_k^+ = P_k(N+1) - P_k(N)$	(For nucleophilic attack)	(6)
$f_k^- = P_k(N) - P_k(N-1)$	(For electrophilic attack)	(7)
$f_k^{0} = \frac{P_k(N+1) - P_k(N-1)}{2}$	(For radical attack)	(8)

where, $P_k(N)$, $P_k(N+1)$ and $P_k(N-1)$ are the natural populations for the atom k in the neutral, anionic and cationic species respectively.

Table 4 displays the most relevant values of the natural population (P(*N*), *P*(*N*-1) and *P*(*N*+1)) with the corresponding values of the Fukui functions $(f_k^+, f_k^- \text{ and } f_k^0)$ of the studied inhibitors. The calculated values of the f_k^+ for all inhibitors are mostly localized on the pyridine ring, namely N₉, C₁₀, C₁₂ and C₁₃, indicating that the pyridine ring will probably be the favorite site for nucleophilic attacks.



Figure 2. The HOMO and the LUMO electrons density distributions of the studied inhibitors computed at B3LYP/6-31G(d,p) level in gas phase

This result is in good agreement with the obtained frontier molecular orbital electron density distribution. However, the values of f_k^+ in Cl-PP and Br-PP are higher than the corresponding ones in H-PP and Me-PP (e.g: Cl-PP and Br-PP $f_k^+(C_{10})=0.139$, in H-PP $f_k^+(C_{10})=0.126$ and in Me-PP $f_k^+(C_{10})=0.107$), which can be a result of the reduced electron density on the pyridine ring in Cl-PP and Br-PP due to the (-I) effect of Cl and Br atoms, respectively.

The results also show that Cl and Br atoms are suitable sites to undergo both nucleophilic and electrophilic attacks, probably allowing them to adsorb easily and strongly on the mild steel surface.

The results presented in Table 4 also show that C_{11} in Me-PP and H-PP, respectively presents the highest values of f_k in comparison to the other studied inhibitors in gas as well as aqueous solution.

Table	4.	Pertinent	natural	populations	and	Fukui	functions	of	the	studied	inhibitors	calculated	at
	E	B3LYP/6-3	31G(d,p)) in gas, <i>G</i> an	d aq	ueous,	A phases						

Inhibitor	Atom k	Phase	P(N)	P(N+1)	P(N-1)	f_k^+	f_k	$f_k^{\ 0}$
Br-PP	N_9	G	7.516	7.664	7.474	0.148	0.042	0.021
		\boldsymbol{A}	7.526	7.679	7.464	0.153	0.062	0.031
	C ₁₀	G	5.973	6.112	5.938	0.139	0.035	0.017
		А	5.980	6.157	5.927	0.177	0.053	0.029
	C ₁₁	G	6.192	6.158	6.129	-0.034	0.063	0.031
		А	6.195	6.171	6.089	-0.024	0.106	0.053
	C ₁₂	G	6.204	6.385	6.199	0.181	0.005	0.002
		А	6.206	6.409	6.201	0.203	0.005	0.002
	C ₁₃	G	6.295	6.408	6.226	0.113	0.069	0.034
		А	6.294	6.449	6.189	0.155	0.105	0.052
	B r ₁₆	G	34.942	35.049	34.776	0.107	0.166	0.083
		A	34.657	35.039	34.801	0.382	-0.144	-0.072
Cl-PP	N_9	G	7.516	7.665	7.473	0.149	0.043	0.021
		\boldsymbol{A}	7.526	7.681	7.463	0.155	0.063	0.031
	C_{10}	G	5.975	6.114	5.940	0.139	0.035	0.017
		\boldsymbol{A}	5.981	6.159	5.929	0.178	0.052	0.026
	C ₁₁	G	6.123	6.097	6.049	-0.026	0.074	0.037
		\boldsymbol{A}	6.126	6.108	6.021	-0.018	0.105	0.052
	C ₁₂	G	6.205	6.385	6.200	0.180	0.005	0.002
		\boldsymbol{A}	6.206	6.410	6.201	0.204	0.005	0.002
	C ₁₃	G	6.295	6.409	6.224	0.114	0.071	0.035
		\boldsymbol{A}	6.294	6.450	6.188	0.156	0.106	0.053
	Cl_{16}	G	17.004	17.093	16.877	0.089	0.127	0.063
		\boldsymbol{A}	17.021	17.090	16.903	0.069	0.118	0.059
H-PP	N_9	G	7.533	7.672	7.489	0.139	0.044	0.022
		\boldsymbol{A}	7.546	7.703	7.482	0.157	0.064	0.032
	C ₁₀	G	5.964	6.090	5.932	0.126	0.032	0.016
		\boldsymbol{A}	5.973	6.148	5.921	0.175	0.052	0.026
	C ₁₁	G	6.321	6.313	6.203	-0.008	0.118	0.059
		\boldsymbol{A}	6.324	6.323	6.170	-0.001	0.154	0.077
	C ₁₂	G	6.190	6.362	6.189	0.172	0.001	0.0005
		\boldsymbol{A}	6.193	6.401	6.195	0.208	-0.002	-0.001
	C ₁₃	G	6.309	6.405	6.225	0.096	0.084	0.042
		A	6.314	6.459	6.188	0.145	0.126	0.063
Me-PP	N_9	G	7.528	7.670	7.480	0.142	0.048	0.024
		\boldsymbol{A}	7.541	7.700	7.476	0.159	0.065	0.032
	C_{10}	G	5.962	6.069	5.924	0.107	0.038	0.019
	_	A	5.972	6.127	5.909	0.155	0.063	0.031
	C ₁₁	G	6.109	6.111	5.985	0.002	0.124	0.062
	~	A ~	6.107	6.108	5.951	0.001	0.156	0.078
	C_{12}	G	6.185	6.369	6.185	0.184	0.000	0.000
	~	A ~	6.187	6.407	6.187	0.220	0.000	0.000
	C ₁₃	G	6.301	6.391	6.223	0.090	0.078	0.039
		A	6.306	6.443	6.190	0.137	0.116	0.058

This can also be related to the electronic substituent effect in position 16. Indeed, the Cl and Br atoms in Cl-PP and Br-PP are directly linked to C_{11} , exposing it to the electron withdrawing effect of Cl and Br.

4. QSAR STUDY

The trends in most of the investigated global descriptors correlate well with the available experimental inhibition efficiencies, namely those of H-PP and Br-PP [9]. We found it interesting to use the Quantitative Structure–Activity Relationships (QSAR) approach to relate the quantum chemical parameters to the observed inhibition efficiency of the studied inhibitors; in an attempt to derive mathematical equations to estimate theoretically the corrosion inhibition efficiencies of these inhibitors [23,36].

Therefore, the non-linear mathematical model [37] is first used to correlate quantum chemical parameters (E_{HOMO} , E_{LUMO} , μ) at different inhibitor concentrations C_i , with the experimental inhibition efficiencies obtained from H-PP and Br-PP [9]. Multiple regressions are performed on inhibition efficiencies of these inhibitors at a concentration range from 5 10⁻⁵ to 10⁻³ M as shown in Table 5.

Inhibitor	Concentration	IE _{exp} % *	IE _{cal} %	
	C / M		Equation (10)	Equation (11)
Br-PP	5×10^{-5}	75	75.50	75.00
	1×10^{-4}	77	86.04	76.97
	5×10^{-4}	80	96.85	80.50
	1x 10 ⁻³	87	98.40	86.15
C1-PP	5x10 ⁻⁵			83.88
	1x 10 ⁻⁴			89.11
	5×10^{-4}			88.45
	1x 10 ⁻³			90.63
H-PP	5×10^{-5}	62	51.06	61.99
	1x 10 ⁻⁴	73	67.60	73.02
	5×10^{-4}	77	91.25	76.49
	1×10^{-3}	83	95.42	83.84
Me-PP	5x10 ⁻⁵			64.70
	1×10^{-4}			83.59
	5×10^{-4}			82.52
	1×10^{-3}			87.26

Table 5. Experimental inhibition efficiencies of H-PP and Br-PP and calculated inhibition efficienciesof the whole inhibitors obtained at different concentrations using equation (10) and (11)

* Inhibiting efficiency determined at 10⁻³ M as reported in [9]

The non linear model has the form:

$$IE_{cal} \% = \frac{(Ax_i + B)C_i}{1 + (Ax_i + B)C_i} \times 100$$
(9)

with A and B are constants obtained by regression analysis; x_j is a quantum chemical index characteristic for the molecule *j* and C_i denotes the inhibitor concentration.

The obtained equation 7 for the non linear model is as follows:

$$IE_{cal} \% = \frac{(-7.84 \times 10^{6} E_{HOMO} + 10^{6} E_{LUMO} + 2.33 \times 10^{7} \mu + 9.38 \times 10^{6}) \times C_{i}}{1 + (-7.84 \times 10^{6} E_{HOMO} + 10^{6} E_{LUMO} + 2.33 \times 10^{7} \mu + 9.38 \times 10^{6}) \times C_{i}} \times 100$$
(10)

The calculated efficiencies from the equation 9, at different concentrations of both inhibitors, H-PP and Br-PP, are reported in Table 5.

The nonlinear method did not give satisfactory results considering the gap between the experimental and calculated efficiencies, clearly distinguished in the allure of the plot (Fig. 3a) correlating the IE_{cal} % obtained by eq. 10 for each concentration with the IEexp%. Indeed, it presents low determination coefficient R²=0.88 and correlation coefficient r=0.94.



Figure 3. Evolution of the calculated efficiencies versus the experimental efficiencies for both H-PP and Br-PP by using a non linear model (a) and by a quadratic model (b)

The quadratic model is used in an attempt to improve the obtained deviations.

$$IE_{cal} \% = 9.06 + \frac{5.97 \times 10^{-4} E_{HOMO}}{C_i} - \frac{4.06 \times 10^{-3} \mu}{C_i} - \frac{6.27 \times 10^{-8} E_{HOMO}}{C_i^2} + \frac{5.35 \times 10^{-7} \mu}{C_i^2} + \frac{1.68 \times 10^{-12} E_{HOMO}}{C_i^3} - \frac{1.90 \times 10^{-11} \mu}{C_i^3}$$
(11)

The developed a quadratic model (Fig. 3b) demonstrates the significance of the model, as shown by the high determination coefficient $R^2=0.995$ which showed that about 99.5% of the variables are considered in the response. Also the results show high correlation coefficient r=0.99, demonstrating a good correlation between the obtained calculated inhibition efficiencies and the corresponding experimental values (Table 5).

The above calculations prompted us to try using both QSAR methods to calculate the corrosion inhibition of Cl-PP and Me-PP, in order to evaluate the possibility of predicting the inhibition efficiency of derivatives resulting of small changes in the pyridine-pyrazole original structure.

The calculated corrosion inhibition efficiencies according to the quadratic model, displayed in Table 5 show that the corrosion inhibition efficiencies of Cl-PP and Me-PP are comparable to those of Br-PP and H-PP respectively, especially at high concentrations. However Cl-PP may be a better inhibitor than Br-PP.

5. CONCLUSION

Using the DFT/B3LYP method with the 6-31G** and the QSAR approach, the corrosion inhibition abilities of four pyridine-pyrazole derivatives are investigated leading to the following conclusions:

1. Most of the studied quantum chemical descriptors correlate well with the available experimental observations.

2. The electronic effect of the substituent at the meta of the pyridine ring markedly affects the performance of the studied inhibitors.

3. The Cl-PP and Br-PP will probably adsorb onto the mild steel surface through the back donating mechanism.

4. The adsorption will probably occur through the pyridine ring in all the inhibitors.

5. According to the QSAR's quadratic model, Cl-PP and Me-PP will probably have the same corrosion inhibitory performance as Br-PP and H-PP, respectively and especially at high concentrations.

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