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DENSITY FUNCTIONAL THEORY OF THE EFFICIENCIES OF 2-PHENYLIMIDAZO[1,2-A]PYRIDINE AND 2-(M-METHOXYPHENYL)IMIDAZO[1,2-A] PYRIMIDINE AS CORROSION INHIBITORS FOR MILD STEEL

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Abstract. Density Functional Theory (DFT) method was used to study the corrosion inhibition characteristics of 2-phenylimidazo[1,2-a]pyridine (2PIP) and 2-(m-methoxyphenyl)imidazo[1,2-a]pyrimidine (2MPIP) on mild steel. Quantum chemical parameters such as highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap, chemical hardness, softness, dipole moment, absolute electronegativity, electrophilicity index and the fraction of electron transferred were calculated and correlated to inhibition efficiency of the studied molecules. Low energy band gaps coupled with structural stabilities should favour the adsorption of protonated molecules on metal surface at low concentrations and before the adsorption equilibrium. However, at high concentrations and towards equilibrium desorption of the protonated would be rapid due charge repulsion and molecular distortion from planarity which would facilitate the adsorption of neutral molecules on metal surface at equilibrium.

Keywords: 2-phenylimidazo[1,2-a]pyridine, 2-(m-methoxyphenyl) imidazo[1,2-a] pyrimidine, corrosion inhibitors, molecular indices, protonation, DFT

Introduction

Corrosion of mild steel has been a major concern in industry because it resulted into huge economic losses and environmental pollution. The use of organic molecules as inhibitors to protect/prevent metal from corrosion in acidic media has attracted the interest of researchers (Bentiss et al., 2009; Obot et al., 2009; Shukla & Quraishi, 2009; Zhang et al., 2012; Wang, 2001; Popova et al., 2003; Khaled, 2003; Musa et al., 2010; Su & Iroh, 1999; Morad & El-Dean, 2006; Bouklah et al., 2006; Mahdavian & Ashhari, 2010; Ebenso et al., 2010; Li et al., 2009; Benabdellah et al., 2011; Elayyachy et al., 2011; Zarrouk et al., 2010; Zarrok et al, 2011). Among organic molecules that have been used as corrosion inhibitors, the most effective are molecules containing π- electron either in triple bond or conjugated double bond and heteroatom such as nitrogen, oxygen, phosphorous and sulphur (Masoud et al., 2010; Ju et al., 2008; Döner et al., 2011; Chen et al., 2011). The inhibitory efficiency is closely related to the inhibitor adsorption ability, the molecular properties, molecular planarity and nature of the interaction between the p-orbital of inhibitors with the d-orbital of iron (Sastry, 1998; Cruz et al., 2001; Bentis et al., 2009; Cruz et al., 2001). The organic compounds that serve as excellent corrosion inhibitors are those which can donate electrons to unoccupied d-orbital of metal surface during coordinate covalent bonds formation as well accept free electrons from the metal surface by using their anti-bonding orbital to form feedback bonds.

Quantum chemical methods have been veritable tools in determining the molecular structure as well as elucidating the electronic structure and reactivity (Kraka & Cremer, 2000). Therefore, it has become a popular practice to carry out quantum chemical calculations in corrosion inhibition studies. Among other methods, Density functional theory (DFT) (Parr & Yang, 1989) has been a very useful method in developing new criteria for rationalizing, predicting and understanding chemical processes. Many of chemical concepts which are now widely used as descriptors of chemical reactivity include electronegativity, chemical hardness, softness quantities Mullikan charges and Fukui function (Cohen, 1996; Awad, 2004; Parr & Yang, 1984; Pearson, 1963; Gece, 2008; Udhayakala et al., 2012a; 2012b; Arshadi et al., 2004). Recently, quantum chemical calculations have been used to study the inhibition mechanism of organic molecules on metal (Lashkari & Arshadi, 2004; Jamalizadeh et al., 2008; 2009; Henriquez-Roman et al., 2005; Gece & Bilgic, 2010; Rodriguez-Valdez et al., 2004; Blajiev & Hubin, 2004).

Recently, 2-phenylimidazo[1,2-a]pyridine (2PIP) and 2-(m-methoxyphenyl) imidazo[1,2-a]pyrimidine (2MPIP) were used as corrosion inhibitors of mild steel in 1.0 M hydrochloric acid solution. Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy techniques were employed in the study (Ghazoui et al., 2012). Therefore, the objective of the present work is to extend the study of the inhibitive properties of 2-phenylimidazo[1,2-a]pyridine and 2-(m-methoxyphenyl) imidazo[1,2-a] pyrimidine using DFT calculations to look for parameters to characterize the inhibition property of inhibitors, which will be helpful to gain insight into the mechanism of the corrosion inhibition (Fig. 1).

Computational method

Density functional theory, Becke's (1993) three-parameter hybrid functional, employing the Lee et al. (1988) correlation functional B3LYP) with 6–31G* basis, set was used for the geometry optimization in order to explore correlation between theoretical and experimental results as implemented in Spartan 06 software package. DFT has been a veritable method to describe the structural nature of the inhibitor in the corrosion process

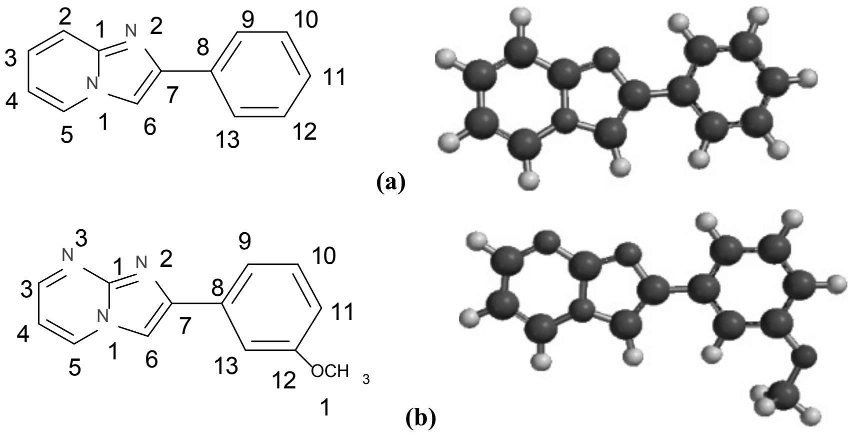

Fig. 1. The molecular structure of (a) 2-phenylimidazo[1,2-a]pyridine and (b) 2-(m-methoxyphenyl) imidazo[1,2-a]pyrimidine

as well as analysing the inhibitor-surface interaction mechanism. DFT is very useful in providing chemical descriptors such as chemical hardness (η), electronegativity (χ), softness (S), electrophilicity index (ω) and local Fukui function indices.

Zhou & Navangul (1990) reported the principle of maximum hardness (absolute hardness) η, for an N-electron system with total energy *E* and η are defined as:

$$\eta = (\frac{\delta^2 E}{\delta N^2})_{v(r)} \approx \frac{1}{2}(IE - EA) \approx \frac{1}{2}(E_{LUMO} - E_{HOMO}) \tag{1}$$

In the formula IE is the vertical ionization energy which is approximated as $-E_{\mathrm{HOMO}}$ and EA for the vertical electron affinity as $-E_{\mathrm{LUMO}}$(Koopmans, 1934). The global softness is the inverse of chemical hardness $(S = \frac{1}{\eta})$. The electron affinity can also be used in combination with ionization energy to give electronic chemical potential *μ,* negative of electron affinity (-χ) defined by Parr and Pearson (Zhou & Navangul, 1990), as the characteristic of electronegativity of molecules:

$$\chi = -\mu = (\frac{\delta E}{\delta N})_{v(r)} \approx \frac{1}{2}(IE + EA) \approx -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \tag{2}$$

The global electrophilicity index ω was introduced by Parr et al. (1999); this is calculated using the electronic chemical potential *μ* and chemical hardness η as

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

According to the definition this index measures the propensity of a species to accept electrons. Domingo et al. (2002) proposed that the high nucleophilicity and electrophilicity of heterocycles corresponds to opposite extremes of the scale of global reactivity indexes. A good, more reactive, nucleophile is characterized by a lower value of μ, ω and in opposite a good electrophile is characterized by a high value of μ, ω.

When considering the interaction of Fe and inhibitor, electrons will flow from lower χ of inhibitor to higher χ of iron metal until equilibrium is reached (i.e., $\mu(Fe) = \mu(inhibitor)$). The fraction of transferred electrons (ΔN) from inhibitor to Fe is given as:

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

The theoretical values for electronegativity (χ_{Fe}) and global chemical hardness (η_{Fe}) of bulk iron are given as 0 and 7.0 eV respectively; these values are used to compute number of electrons transfer (Yang & Parr, 1985). The local reactivity is evaluated by using Fukui function which can be calculated using the finite difference approximation as follows (Yang & Parr, 1985):

$f^+ = q_k(N+1) - q_k(N)$ for nucleophilic attack
$f^- = q_k(N) - q_k(N-1)$ for electrophilic attack
where $q_k(N)$, $q_k(N+1)$ and $q_k(N-1)$ are the electronic population of the atom k in neutral, anionic and cationic species.

Results and discussion

Molecular reactivity

The frontier molecular orbital and Fukui functions were used to analyse the reactivity of the studied molecules. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are related to the electron donating and accepting ability of a molecule. Molecules with high E_{HOMO} would have better tendency to donate electrons to acceptor molecules with low $E_{LUMO.}$ Increase in E_{HOMO} values facilitate adsorption; thus enhance the inhibition efficiency. Therefore, the binding ability of the inhibitor to the metal surface should increase with increasing of the HOMO and decreasing of the LUMO energy values (Udhayakala et al., 2012a; 2012b). However, in this study 2MPIP with lower E_{HOMO} (-5.65 eV) and E_{LUMO} (-1.57 eV) presented better inhibitory efficiency as compared to 2PIP (E_{HOMO} -5.56 eV and E_{LUMO} = -1.06 eV). This agreed with the trend observed in DFT study on Methylene blue dye, Crystal violet dye and Indigo blue dye corrosion inhibition efficiency (%IE) (Oguike et al., 2013).

Another important parameter to measure reactivity of the inhibitor molecule towards the adsorption on the metallic surface is the energy gap, ΔE ($\Delta E = E_{\mathrm{LUMO}} – E_{\mathrm{HOMO}}$); decreasing in ΔE of the molecule leads to increasing in the %IE of the molecule because lesser/lower energy would be required to remove an electron from the last occupied orbital. A molecule with a low energy gap is usually more polarisable with high chemical activity, low kinetic stability and high softness value (Fleming, 1976); thus 2MPIP with low ΔE value (4.08 eV), higher dipole moment (5.65 Debye) and high softness (0.490) has better performance as a corrosion inhibitor (Ghazoui et al., 2012).

Table 1. Calculated molecular parameters at B3LYP/6-31G*

Parameters	2PIP	2MPIP
E_T (N) (au)	-610.912763	-741.470226
E_T (N+1) (au)	-610.897409	-741.471840
E_T (N-1) (au)	-610.653169	-741.209485
E_{HOMO} (eV)	-5.56	-5.65
E_{LUOMO} (eV)	-1.06	-1.57
E_{HOMO} -E_{LUMO}(eV)	4.50	4.08
Dipole moment (Debye)	3.13	5.65
Η	2.25	2.04
Χ	3.31	3.61
S	0.444	0.490
ω	2.435	3.194
ΔN	0.820	0.831
*Inhibition efficiency (%IE)	95.30	98.80

**Inhibition efficiency was taken from (Ghazoui et al., 2012)*

The global parameters such as chemical hardness (η), chemical potential (μ) and electronegativity (χ) were calculated as shown in Table 1. The chemical hardness and softness are important properties to measure the molecular stability and reactivity. A hard molecule has a large energy gap and a soft molecule has a small energy gap. The inhibitor with the least value of global chemical hardness (i.e., the highest value of global softness) is expected to have the highest ability to donate electrons; thus high inhibition efficiency (Udhayakala et al., 2012a; 2012b; Lukovits et al., 2001). Therefore, the 2MPIP with low η value of 2.04 eV as compared to 2.25 eV for 2PIP has highest %IE. On the other hand, electronegativity denotes electron-accepting ability of a molecule shows that the electron-donating capability of 2MPIP molecule is higher than that of 2PIP. The number of electrons transferred during the adsorption (ΔN) for 2PIP and 2MPIP are 0.820 and

0.831 respectively. According to Lukovits, if $\Delta N < 3.6$ the inhibition efficiency increases with increasing electron-donating capacity on metal surface (Lukovits et al., 2001), the ΔN values correlate strongly with experimental inhibition efficiencies.

Mulliken population analysis is mostly used for the calculation of the charge distribution over the whole molecule which has been a useful parameter to estimate the adsorption centres of inhibitors. The Mulliken charges on N1 and N2 for 2PIP are -0.486 and -0.578*e* respectively. For 2MPIP, Mulliken charges on N1, N2, N2 and O1 are -0.483, -0.555, -0.457 and -0.511*e* respectively (Table 2). It is generally agreed that the more negatively charged a heteroatom, the more it can be adsorbed on the metal surface (Breket et al., 2002); therefore zones containing N and O are most probable sizes for adsorption of the inhibitor on the metal surface.

In addition, Fukui functions revealed the local site for either electrophilic or nucleophilic attack on the molecules (Table 2). The f^- measures reactivity of an atom with respect

Table 2. Fukui indices for nucleophilic and electrophilic attacks on 2PIP and 2MPIP

2PIP						2MPIP					
atom	q_kN	q_kN+1	q_kN-1	f_k^+	f_k^-	atom	q_kN	q_kN+1	q_kN-1	f_k^+	f_k^-
C1	0.546	0.534	0.585	-0.012	-0.039	C1	0.690	0.658	0.732	-0.032	-0.042
C2	-0.179	-0.250	-0.169	-0.071	-0.010	C3	0.042	-0.008	0.075	-0.050	-0.033
C3	-0.123	-0.143	-0.087	-0.020	-0.036	C4	-0.198	-0.188	-0.189	0.010	-0.009
C4	-0.186	-0.185	-0.176	0.001	-0.010	C5	0.098	-0.013	0.117	-0.111	-0.019
C5	0.073	-0.021	0.103	-0.094	-0.030	C6	-0.016	0.039	0.069	**0.055**	-0.085
C6	-0.023	-0.048	0.092	-0.025	-0.115	C7	0.186	0.162	0.197	-0.024	-0.011
C7	0.173	0.151	0.198	-0.022	-0.025	C8	0.098	0.088	0.093	-0.010	0.005
C8	0.102	0.082	0.098	-0.020	0.004	C9	-0.178	-0.194	-0.117	-0.016	-0.061
C9	-0.171	-0.193	-0.135	-0.022	-0.036	C10	-0.135	-0.138	-0.122	-0.003	-0.013
C10	-0.133	-0.135	-0.123	-0.002	-0.010	C11	-0.168	-0.202	-0.118	-0.034	-0.050
C11	-0.126	-0.164	-0.095	-0.038	-0.031	C12	0.376	0.361	0.398	-0.015	-0.022
C12	-0.139	-0.141	-0.130	-0.002	-0.009	C13	-0.257	-0.279	-0.228	-0.022	-0.029
C13	-0.178	-0.194	-0.150	-0.016	-0.028	N1	-0.463	-0.444	-0.478	0.019	0.015
N1	-0.486	-0.458	-0.505	**0.028**	**0.019**	N2	-0.555	-0.610	-0.534	-0.055	-0.021
N2	-0.578	-0.628	-0.535	-0.050	-0.043	N3	-0.457	-0.559	-0.433	-0.102	-0.024
H2	0.157	0.077	0.218	-0.080	-0.061	H3	0.153	0.064	0.208	-0.089	-0.055
H3	0.142	0.061	0.212	-0.081	-0.070	H4	0.154	0.067	0.208	-0.087	-0.054
H4	0.145	0.066	0.211	-0.079	-0.066	H5	0.173	0.089	0.217	-0.084	-0.044
H5	0.164	0.088	0.223	-0.076	-0.059	H6	0.159	0.101	0.216	-0.058	-0.057
H6	0.158	0.103	0.237	-0.055	-0.079	H9	0.165	0.134	0.230	-0.031	-0.065
H9	0.161	0.122	0.204	-0.039	-0.043	H10	0.133	0.083	0.202	-0.050	-0.069
H10	0.129	0.071	0.189	-0.058	-0.060	H11	0.137	0.082	0.213	-0.055	-0.076
H11	0.127	0.062	0.193	-0.065	-0.066	H13	0.126	0.095	0.161	-0.031	-0.035
H12	0.126	0.068	0.185	-0.058	-0.059	O1	-0.511	-0.528	-0.459	-0.017	-0.052
H13	0.118	0.077	0.158	-0.041	-0.040	C14	-0.211	-0.192	-0.245	0.019	**0.034**
						H14a	0.149	0.137	0.184	-0.012	-0.035
						H14b	0.170	0.133	0.221	-0.037	-0.051
						H14c	0.149	0.137	0.184	-0.012	-0.035

to electrophilic attack (i.e. the characteristic of the molecule to donate electrons) and f^+ measures reactivity related to nucleophilic attack (i.e., the propensity of the molecule to accept electrons). The local reactivity of 2PIP by mean of condensed Fukui functions showed that the most probable site for nucleophilic and electrophilic attack was on the same atom, N1. C6 and C14 atoms were most probably sites for nucleophilic and electrophilic attack for 2MPIP respectively (Table 2).

Molecular properties of protonated 2PIP and 2MPIP

The corrosion of a metal and chemical inhibitory process usually occurs in acidic medium; therefore protonation of the studied molecules was performed to deepen our understanding on corrosion inhibitory processes involving the studied molecules. The protonation sites that led to low molecular energy were on N1 and N2 for 2PIP (i.e. 2PIPH$^+$, N2 and 2PIPH$^+$ N1, N2) and N2 and N3 for 2MPIP (2MPIPH$^+$, N2 and 2MPIP2H^{++}, N2, N3); although in 2MPIP there is a possibility of adding three protons to the molecule but lowest energy structures obtained are considered (Table 3). The calculated N1-C6 and N2-C7 bond lengths were 1.393 and 1.391Å for 2PIPH$^+$ (N2) and 1.436 and 1.488Å for 2PIP2H^{++} (N1, N2) as compared to 1.375 and 1.371Å for 2PIP, respectively. These bonds were 1.390Å for 2MPIPH$^+$ (N2) and 1.382 and 1.412Å for 2MPIP2H^{++} (N2, N3) compared to 1.372 and 1.370Å for neutral 2MPIP. This showed N1-C6 and N2-C7 bonds were elongated, thus experienced bond localization. However, C6-C7 and C7-C8 bonds were shortened in protonated as compared to neutral inhibitors.

Table 3. Selected bond length (Å) for 2PIP and 2MPIP

	E_{HOMO}	E_{LUMO}	ΔE	η	S	C_1-N_2	N_1-C_6	N_2-C_7	C_6-C_7	C_7-C_8
2PIP	-5.56	-1.06	4.50	2.25	0.44	1.327	1.375	1.371	1.390	1.470
2PIPH$^+$ (N2)	-9.85	-5.56	4.29	2.15	0.47	1.357	1.393	1.391	1.371	1.461
2PIP2H^{++} (N1,N2)	-13.45	-11.93	1.52	0.76	1.32	1.314	1.436	1.488	1.359	1.444
2MPIP	-5.65	-1.57	4.08	2.04	0.49	1.322	1.372	1.370	1.391	1.470
2MPIPH$^+$ (N2)	-9.18	-6.08	3.10	1.55	0.65	1.351	1.390	1.390	1.376	1.458
2MPIP2H^{++} (N2,N3)	-12.26	-11.00	1.26	0.63	1.59	1.333	1.382	1.412	1.386	1.438

Planarity of molecules is an important parameter to be considered in adsorption of inhibitor on metal surface. For neutral molecules, a complete planarity is observed in contrast to the protonated forms, suggesting that the neutral molecules have greater capability of corrosion inhibition. For instance, N2C7C8C9 and N2C7C8C13 bond angles

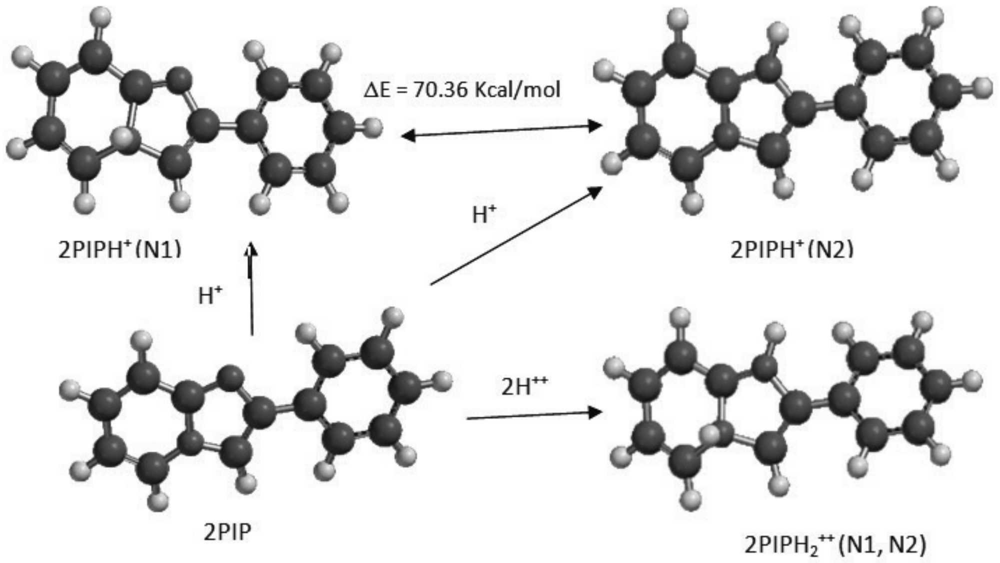

Fig. 2. Optimized geometries of first and second protonation of 2PIP

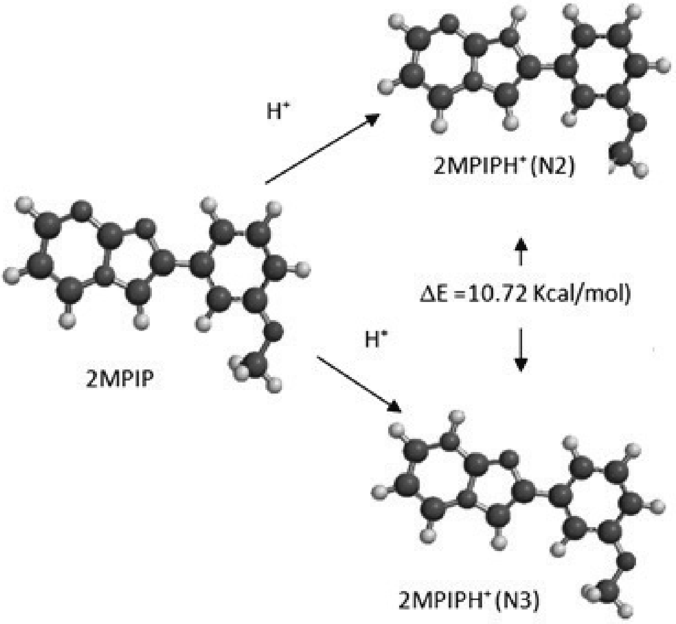

Fig. 3. Optimized geometries of first protonation of 2MPIP

were -29.10° and 151.20° in 2PIPH^{+} (N2), -23.46° and 157.68° in 2PIP2H^{++} (N1,N2), 26.06° and -154.28° in 2MPIPH^{+} (N2) and -16.36° and 164.44° in 2MPIP2H^{++} (N2,N3) as compared to 0.00° and 180.00° in both 2PIP and 2MPIP. However, the calculations show that more stable structures were obtained when protonation occurred at N2, this resulted into 70.36 kcal/mol energy difference between 2PIPH^{+} (N2) and 2PIPH^{+} (N1) moieties (Fig. 2). Second protonation at N1 (i.e. 2PIP2H^{++} (N1,N2)) further reduced the energy by 62.06 kcal/mol as compared 2PIPH^{+} (N2). The first protonation of 2MPIP at N2 resulted in lower energy by 10.72 kcal/mol compared to the protonation at N3 (Fig. 3). The stable structure for second protonation occurred at N2 and N3 (2MPIP2H^{++} (N2,N3)). This brought about reduction of energy by 69.09 kcal/mol and 69.41 as compared to 2MPIP2H^{++} (N1,N2) and 2MPIP2H^{++} (N1,N3) respectively (Fig. 4); thus the proton addition was preferred at amine nitrogen rather than the benzimidazole nitrogen.

Molecular properties of the protonated

The frontier molecular orbital maps comprising of HOMO, HOMO-1, LUMO and LUMO+1 for the neutral and protonated molecules were displayed in Fig. 5. The analysis of electronic properties of the protonated molecules revealed changes in chemical properties such as electron-donating capability of the inhibitors to the metal. The E_{HOMO}-E_{LUMO},

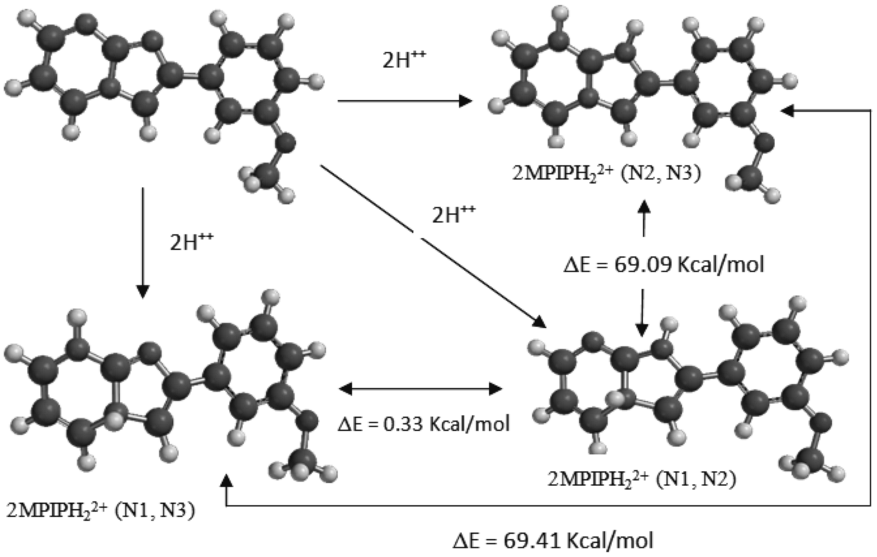

Fig. 4. Optimized geometries of 2H^{++} protonation of 2MPIP

Δ*E* of the neutral, single protonation and double protonation were 4.50, 4.29 and 1.52 eV for 2PIP, 2PIPH^{+} and 2PIP2H^{++} and 4.08, 3.10 and 1.26 eV for 2MPIP, 2MPIPH^{+} and 2MPIP2H^{++} respectively. The E_{HOMO}-E_{HOMO-1} or E_{LUMO}-E_{LUMO+1} decreases or increases with increase in number of protons for protonation (Fig. 5). Low energy gaps coupled with structural stabilities should favour the adsorption of protonated species on metal surface. Therefore, it is suggested that at low concentrations and before the equilibrium more of protonated species will be adsorbed on the metal surface. However, at high concentrations and towards equilibrium desorption of the protonated would be rapid from metal surface due charge repulsion and molecular distortion of the molecules from planarity; this facilitates the adsorption of neutral molecules on metal surface at equilibrium.

Conclusions

(1) The electronic and molecular properties calculated for 2-phenylimidazo[1,2-a] pyridine and 2-(*m*-methoxyphenyl)imidazo[1,2-a]pyrimidine using DFT method correlated with the inhibitory capability of the studied molecules.

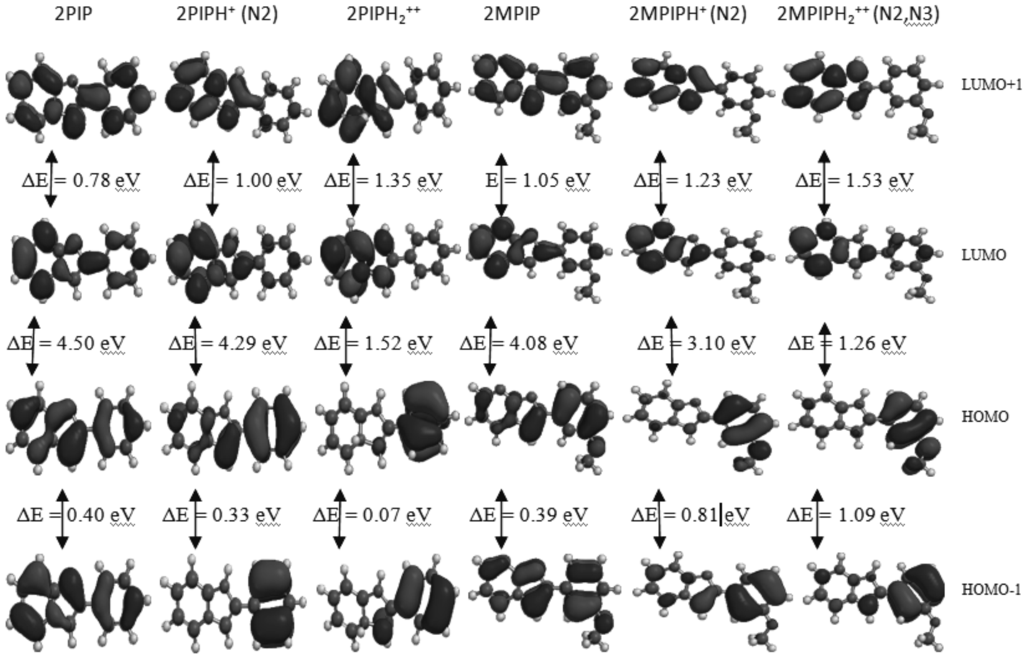

Fig. 5. The frontier molecular orbitals; HOMO, HOMO+1, LUMO and LUMO+1 of neutral and protonated 2PIP and 2MPIP molecules

(2) The chemical hardness, electronegativity, energy band gap and the fraction of electron transferred confirms that the inhibition efficiency in the order 2MPIP > 2PIP; (2) Complete planarity of neutral molecules in contrast to the protonated forms suggested that the neutral molecules have greater capability of corrosion inhibition.

(3) The protonated species presented lower band gap and higher stability than the neutral molecules. Therefore, low energy gaps coupled with structural stabilities should favour the adsorption of protonated species on metal surface; it is suggested that at low concentrations and before the adsorption equilibrium is reached more of protonated species will be adsorbed on the metal surface.

(4) The proton addition is preferred at amine nitrogen rather than the benzimidazole nitrogen.

REFERENCES

Arshadi, M.R., Lashgari, M. & Parsafar, G.A. (2004). Cluster approach to corrosion inhibition problems: interaction studies. *Mater. Chem. Phys., 86*, 311–314.

Awad, M.K. (2004). Semiempirical investigation of the inhibition efficiency of Thiourea derivatives as corrosion inhibitors. *J. Electroanal. Chem., 567*, 219-225.

Becke, A.D. (1993). Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys., 98*, 5648-5652.

Benabdellah, M., Yahyi, A., Dafali, A., Aouniti, A., Hammouti, B. & Ettouhami, A. (2011). Corrosion inhibition of steel in molar HCl by triphenyltin2-thiophene carboxylate. *Arab. J. Chem., 4,* 343-347.

Bentiss, F., Jama, C., Mernari, B., El Attari, H., El Kadi, L., Lebrini, M., Traisnel, M. & Lagrenée, M. (2009). Corrosion control of mild steel using 3, 5-bis (4-methoxyphenyl)-4-amino-1, 2, 4-triazole in normal hydrochloric acid medium. *Corrosion Sci.*, *51*, 1628–1635.

Blajiev, O. & Hubin, A. (2004). Inhibition of copper corrosion in chloride solutions by amino-mercapto-thiadiazole and methyl-mercapto-thiadiazole: an impedance spectroscopy and a quantum chemical investigation. *Electrochim. Acta, 49*, 2761–2770.

Bouklah, M., Benchat, N., Hammouti, B., Aouniti, A. & Kertit, S. (2006). Thermodynamic characterisation of steel corrosion and inhibitor adsorption of pyridazine compounds in 0.5 M H_2SO_4. *Mater. Lett., 60*, 1901–1905.

Breket, G., Hur, E. & Ogretir, C. (2002). Quantum chemical studies of some pyridine derivatives as corrosion inhibitor in acidic medium. *J. Mol. Struct. THEOCHEM, 578*, 79-88.

Chen, W., Luo, H.Q. & Li, N.B. (2011). Inhibition effects of 2,5-dimercapto-1,3,4-thiadiazole on the corrosion of mild steel in sulphuric acid solution. *Corrosion Sci., 53,* 3356–3365.

Cohen, M.H. (1996). Strengthening the foundations of chemical reactivity theory (pp. 143-173). In: Nalewajski, R.F. (Ed.). *Density functional theory IV - theory of chemical reactivity*. Heidelberg: Springer.

Cruz, J., Martinez-Aguilera, L.M.R., Salcedo, R. & Castro, M. (2001). Reactivity properties of derivatives of 2-imidazoline: an ab initio DFT study. *Intern. J. Quantum Chem., 85,* 546-556

Cruz, J., Pandiyan, T. & Garcia-Ochoa, E.A. (2005). A new inhibitor for mild carbon steel: electrochemical and DFT studies. *J. Electroanal. Chem., 583*, 8-16.

Domingo, L. R., Aurell, M., Contreras, M. & Perez, P. (2002). Quantitative characterization of the local electrophilicity of organic molecules: understanding the regioselectivity on Diels−Alder reactions. *J. Phys. Chem. A., 106,* 6871-6876.

Döner, A., Solmaz, R., Özcan, M. & Kardas, G. (2011). Experimental and theoretical studies of thiazoles as corrosion inhibitors for mild steel in sulphuric acid solution. *Corrosion Sci., 53*, 2902–2913.

Ebenso, E.E., Obot, I.B. & Murulana, L.C. (2010). Quinoline and its derivatives as effective corrosion inhibitors for mild steel in acidic medium. *Intern. J. Electrochem. Sci., 5,* 1574–1586.

Elayyachy, M., Hammouti, B., El Idrissi, A. & Aouniti, A. (2011). Adsorption and corrosion inhibition behavior of C38 steel by one derivative of quinoxaline in 1 M HCl. *Portugaliae Electrochim. Acta, 29,* 57-68.

Fleming, I. (1976). *Frontier oritals and organic chemical reactions*. New York: John Wiley & Sons.

Gece, G. (2008). (2008). The use of quantum chemical methods in corrosion inhibitor studies. *Corrosion Sci., 50,* 2981–2992.

Gece, G. & Bilgic, S. (2010). A theoretical study of some hydroxamic acids as corrosion inhibitors for carbon steel. *Corrosion Sci., 52*, 3304-3308.

Ghazoui, A., Saddik, R., Benchat, N., Guenbour, M., Hammouti, B., Al-Deyab, S.S. & Zarrouk, A. (2012). Comparative study of pyridine and pyrimidine derivatives as corrosion inhibitors of C38 steel in molar HCl. *Intern. J. Electrochem. Sci., 7*, 7080 – 7097

Henriquez-Roman, J.H., Padilla-Campos, L., Paez, M.A., Zagal, J.H., Rubio, M.A., Rangel, C.M., Costamagna, J. & Cardenas-Jiron, G. (2005). The influence of aniline and its derivatives on the corrosion behaviour of copper in acid solution: a theoretical approach. *J. Mol. Struct. THEOCHEM, 757*, 1–7.

Jamalizadeh, E., Jafari, A.H. & Hosseini, S.M.A. (2008). Semi-empirical and ab initio quantum chemical characterisation of pyridine derivatives as HCl inhibitors of aluminium surface. *J. Mol. Struct. THEOCHEM, 870*, 23–30.

Jamalizadeh, E., Hosseini, S.M.A. & Jafari, A.H. (2009). Quantum chemical studies on corrosion inhibition of some lactones on mild steel in acid media. *Corrosion Sci., 51,* 1428–1435

Ju, H., Kai, Z.-P. & Li, Y. (2008). Aminic nitrogen-bearing polydentate Schiff base compounds as corrosion inhibitors for iron in acidic media: a quantum chemical calculation. *Corrosion Sci., 50,* 865–871.

Khaled, K.F. (2003). The inhibition of benzimidazole derivatives on corrosion of iron in1

M HCl solutions. *Electrochim. Acta, 48*, 2493-2503.

Koopmans, T. (1934). Ordering of wave functions and eigenvalues to the individual electrons of an atom. *Physica, 1,* 104-113.

Kraka, E. & Cremer, D. (2000). Computer design of anticancer drugs. *J. Amer. Chem. Soc., 122*, 8245–8264.

Lashkari, M. & Arshadi, M.R. (2004). DFT studies of pyridine corrosion inhibition electrical double layer: solvent, substrate, and electric field effects. *Chem. Phys. 299*, 131–137.

Lee, C., Yang, W. & Parr, R.G. (1988). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B, 37*, 785-789.

Li, X., Deng, S., Fua, H. & Li, T. (2009). Adsorption and inhibition effect of 6-benzylaminopurine on cold rolled steel in 1.0 M HCl. *Electrochim. Acta, 54*, 4089–4098.

Lukovits, I, Kalman, E. & Zucchi, F. (2001). Corrosion inhibitors—correlation between electronic structure and efficiency. *Corrosion, 57,* 3-8.

Mahdavian, M. & Ashhari, S. (2010). Corrosion inhibition performance of 2-mercaptobenzimidazole and 2-mercaptobenzoxazole compounds for protection of mild steel in hydrochloric acid solution. *Electrochim. Acta, 55*, 1720–1724.

Masoud, M.S., Awad, M.K., Shaker, M.A. & El-Tahawy, M.M.T. (2010). The role of structural chemistry in the inhibitive performance of some aminopyrimidines on thecorrosion of steel. *Corrosion Sci., 52*, 2387–2396.

Morad, M.S. & El-Dean, A.M.K. (2006). 2,2 0-Dithiobis(3-cyano-4, 6-dimethylpyridine): a new class of acid corrosion inhibitors for mild steel. *Corrosion Sci., 48*, 3398–3412.

Musa A.Y., Kadhum, A.A.H., Mohamad A.B. & Takriff, M.S. (2010). Experimental and theoretical study on the inhibition performance of triazole compounds for mild steel corrosion. *Corrosion Sci., 52*, 3331–3340.

Obot, I.B., Obi-Egbedi, N.O. & Umoren, S.A. (2009). Drugs as corrosion inhibitors for aluminium in 0.1 M HCl. *Corrosion Sci., 51*, 1868–1875.

Oguike, R.S., Kolo, A.M., Shibdawa, A.M. & Gyenna, H.A. (2013). Density functional theory of mild steel corrosion in acid midie using dyes as inhibitor: adsorption onto Fe(110) from gas phase. *ISRN Phys. Chem., 2013*, art. no. 175910.

Parr, R.G. & Yang, W. (1984). Density functional approach to the frontier-electron theory of chemical reactivity. *J. Amer. Chem. Soc., 106*, 4049-4050.

Parr, R.G. & Yang, W. (1989). *Density functional theory of atoms and molecules*. New York: Oxford University Press.

Parr, R.G., Szentpaly, L. & Liu, S. (1999). Electrophilicity index. *J. Amer. Chem. Soc., 121,* 1922-1924.

Pearson, R.G. (1963). Hard and soft acids and bases. *J. Amer. Chem. Soc., 85*, 3533-3543.

Popova, A., Christov, M. & Deligeorgiev, T. (2003). Influence of the molecular structure on the inhibitor properties of benzimidazole derivatives on mild steel corrosion in 1 M hydrochloric acid. *Corrosion, 59*, 756-764.

Rodríguez-Valdez, L.M., Martínez-Villafane, A. & Glossman-Mitnik, D. (2004). CHIH-DFT determination of the molecular structure, infrared and ultraviolet spectra of potentially organic corrosion inhibitors. *J. Mol. Struct. THEOCHEM, 681*, 83–88.

Sastry, V.S. (1998). *Corrosion inhibitors: principles and applications*. New York: John Wiley & Sons.

Shukla S.K. & Quraishi, M.A. (2009). 4-Substituted anilinomethylpropionate: new and efficient - corrosion inhibitors for mild steel. *Corrosion Sci., 51,* 1007–1011.

Su, W. & Iroh, J.O. (1999). Electropolymerization of pyrrole on steel substrate in the presence of oxalic acid and amines. *Electrochim. Acta, 44,* 2173–2184.

Udhayakala, P., Rajendiran, T.V. & Gunasekaran, S. (2012a). Quantum chemical studies on the efficiencies of vinyl imidazole derivatives as corrosion inhibitors for mild steel. *J. Adv. Scient. Res., 3*, 37-44.

Udhayakala, P., Rajendiran, T.V. & Gunasekaran, S. (2012b). Theoretical approach to the corrosion inhibition efficiency of some pyrimidine derivatives using DFT method. *J. Comput. Methods Mol. Des., 2*, 1-15.

Wang L. (2001). Evaluation of 2-mercaptobenzimidazole as corrosion inhibitor for mild steel in phosphoric acid. *Corrosion Sci. 43*, 2281-2289.

Yang, W. & Parr, R. (1985). Hardness, softness, and the Fukui function in the electronic theory of metals and catalysis. *Proc. Nat. Acad. Sci. USA, 82,* 6723–6726.

Zarrok, H., Saddik, R., Oudda, H., Hammouti, B., El Midaoui, A., Zarrouk, A., Benchat, N. & Ebn Touhami, M. (2011). 5-(2-chlorobenzyl)-2,6-dimethylpyridazin-3-one: an efficientInhibitor of C38 steel corrosion in hydrochloric acid. *Pharma Chemica, 3*, 272-282.

Zarrouk, A., Warad, I., Hammouti, B., Dafali, A, Al-Deyab, S.S. & Benchat, N. (2010). The effect of temperature on the corrosion of Cu/HNO_3 in the presence of organic inhibitor: part-2. *Intern. J. Electrochem. Sci., 5*, 1516-1526.

Zhang, F., Tang, Y., Cao, Z., Jing, W., Wu, Z. & Chen, Y. (2012). Performance and theoretical study on corrosion inhibition of 2-(4-pyridyl)-benzimidazole for mild steel in hydrochloric acid. *Corrosion Sci., 61,* 1–9.

Zhou, Z. & Navangul, H.V. (1990). Absolute hardness and aromatisity: MNDO study of benzenoid hydrocarbons. *J. Phys. Org. Chem., 3*, 784-788.

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