Additional Halogen Group (F, Cl, and Br) to 2-Phenyl-imidazole[1,2α]pyridine on Corrosion Inhibition Properties: A Computational Study

IOP Conf. Series: Materials Science and Engineering **288** (2017) 012033 doi:10.1088/1757-899X/288/1/012033

Additional Halogen Group (F, Cl, and Br) to 2-Phenyl-imidazole[1,2α]pyridine on Corrosion Inhibition Properties: A Computational Study

C D D Sundari[1*], S Setiadji[2], M A Ramdhani[3], A L Ivansyah[2,4] and N I T Widhiasari[2]

[1]Department of Chemistry Education, UIN Sunan Gunung Djati Bandung, Indonesia
[2]Department of Chemistry, UIN Sunan Gunung Djati Bandung, Indonesia
[3]Department of Informatics, UIN Sunan Gunung Djati Bandung, Indonesia
[4]Department of Chemistry, Institut Teknologi Bandung (ITB), Indonesia

*citra@uinsgd.ac.id

Abstract. Imidazole compound and its derivatives have good corrosion inhibition properties towards metals and alloys. One of its derivative, 2-Phenyl-imidazole[1,2α]pyridine, has a good potential as corrosion inhibitor considering its structure. In this paper, computational studies on 2-phenylimidazole[1,2α]pyridine and the effect of halogen group (F, Cl, and Br) on its corrosion inhibition properties has been performed. The calculations were carried out using Restricted Hartree-Fock (RHF) method with 6-31+G(d,p) basis set in gas phase. Structural optimization shows that all compounds studied in this paper have planar structure. Negative Mulliken charge possessed by nitrogen, halogen, and several carbon atoms indicates the possible sites of adsorption toward metal surface. Calculation results predict that 2-(4-bromophenyl) imidazole[1,2α] pyridine will be a better corrosion inhibitor from the value of electronic properties compared to the rest of the compounds. This compound has highest HOMO energy level and dipole moment, and also has lowest energy gap, LUMO energy, and global hardness. This results was mainly caused by the larger atomic size of bromine atom and the larger difference of electronegativity value between nitrogen atom and bromine atom compared to chlorine and fluorine atoms. The larger difference in electronegativity will results in larger polarity and the larger atomic size will results in lower global hardness.

1. Introduction

Utilization of corrosion inhibitor is an effective way to decrease corrosion rate in the surface of metal, especially iron. Corrosion inhibitor originated from organic compound has attracted more interest due to its environment-friendly nature compared to inorganic inhibitor. Corrosion inhibitor can slower the corrosion rate because inhibitor compound can be adsorbed to metal surface, forming a thin layer of inhibitor which preventing contact between metal surface and corrosion media. Previous research show that heteroatom of the active group such as N, O, P, and S in the inhibitor molecule contribute to positive effects towards corrosion inhibition efficiency, because these atoms usually become adsorption site to the metal surface [1-7].

Computational calculation is a research method that can be used to investigate and predict corrosion inhibition properties of a molecule. This method has been widely used to study various

topics in chemistry research such as determination of molecular properties, reaction mechanism, etc, from electronic structure levels [8,9,10,11,12]. Molecular structure and its electronic properties can be obtained by means of computational calculations. The nature of molecular orbitals including the energy and density of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are affecting the activity of inhibitors. The activity of inhibitor towards iron surface also can be studied via the hard-soft acid-base (HSAB) theory [13].

Imidazole compound and its derivatives are relatively nontoxic, environmental-friendly, and have a good corrosion inhibition properties towards metals and alloys [14-16]. One of imidazole derivative, i.e. 2-Phenyl-imidazole[1,2α]pyridine, has a good potential as corrosion inhibitor considering from its structure. This compound has lone pairs in nitrogen atoms, conjugated π electrons, and planar structure which support its adsorption to metal surface. The aim of this paper is to investigate molecular structure and electronic properties of 2-phenyl-imidazole[1,2α]pyridine and the effect of additional halogen substituent (F, Cl, Br) to the compound towards its electronic properties and corrosion inhibition efficiency. Computational study of these compounds has not been carried out so far. This study is expected to help scientist in selecting corrosion inhibitor candidate to be tested experimentally.

2. Methods

In this research, ab initio calcullations were carried out on four potential inhibitor compounds, i.e. 2-phenylimidazole[1,2α]pyridine (PIP), 2-(4-fluorophenyl)imidazole[1,2α]pyridine (4-FPIP), 2-(4-chlorophenyl)imidazole[1,2α]pyridine (4-ClPIP), 2-(4-bromophenyl)imidazole[1,2α]pyridine (4-BrPIP) at Restricted Hartree Fock (RHF) level of theory and 6-31+G(d,p) basis set in gas phase using Firefly 8.2.0 [17] software package. The initial coordinate of atoms in the molecules were generated using Avogadro 1.0 [18]. The molecular structures were optimized until minimum energy is reached without negative frequencies, and then the electronic properties were determined i.e. Mulliken atomic charges, HOMO/LUMO energy gap (E_{GAP}), ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η), and dipole moment (D). The optimized molecular structures were visualized using Chemcraft 1.8 [19].

Ionization potential (I) and electron affinity (A) were related to HOMO energy (E_{HOMO}) and LUMO energy (E_{LUMO}) according to Koopman's theorem [20] according to equations (1) and (2):

$$I = -E_{HOMO} \quad (1)$$

$$A = -E_{LUMO} \quad (2)$$

Electronegativity (χ) and global hardness of the inhibitor molecules were given by equation (3) and (4) [21]:

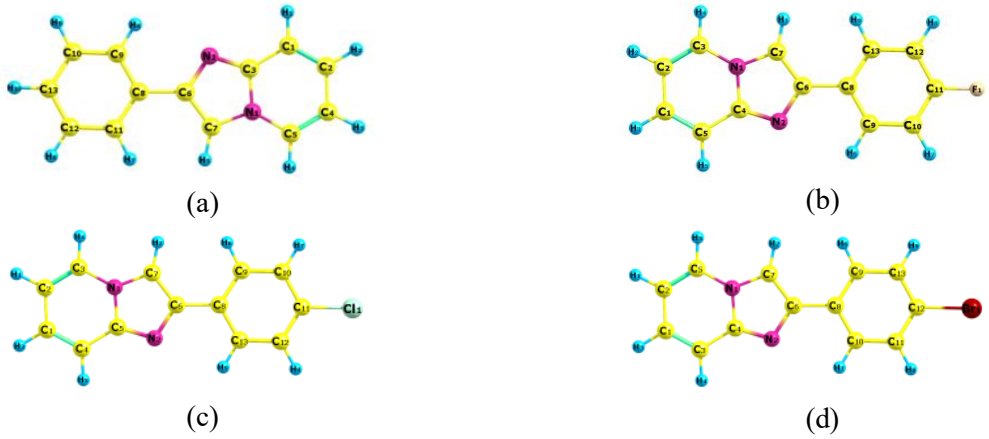
$$\mathrm{X} = \frac{I+A}{2} \quad (3)$$

$$\eta = \frac{I-A}{2} \quad (4)$$

3. Results and discussion

3.1. Molecular Structure

Optimized structure gives structural parameter information such as bond lengths and dihedral angles. Bond length between atoms in the optimized molecular structure of PIP, 4-FPIP, 4-ClPIP, and 4-BrPIP compounds are listed in table 1. The resulting bond lengths were slightly larger than reference (experimental) values [22], but in a comparable range. C-C and C-N bond lengths in delocalized system were in the range of 1.3-1.4 Å, while C-H bond lengths were in 0.9-1.1 Å range. C-F, C-Cl and C-Br bond length were increasing respectively, i.e. 1.334 Å, 1.744 Å, and 1.895 Å due to the difference of halogen atomic radius. Dihedral angles for atoms in the cyclic system for all compounds were 0° and 180° which indicates that all compounds studied were planar. Optimized 2-dimensional structures for PIP, 4-FPIP, 4-ClPIP, and 4-BrPIP can be seen in figure 1.



(a) (b) (c) (d)

Figure 1 Optimized molecular structure of (a) PIP, (b) 4-FPIP, (c) 4-ClPIP, and (d) 4-BrPIP

Table 1. Interatomic bond lengths in the structure of (a) PIP, (b) 4-FPIP, (c) 4-ClPIP, and (d) 4-BrPIP.

Bond type	Bond length (Å)				
	PIP	4-FPIP	4-ClPIP	4-BrPIP	Reference [22]
$_{1}$C-$_{16}$H	1.075	1.075	1.075	1.075	0.93
$_{5}$C-$_{6}$N	1.371	1.374	1.393	1.393	1.341
$_{12}$C-F	-	1.334	-	-	-
$_{12}$C-Cl	-	-	1.744	-	-
$_{12}$C-Br	-	-	-	1.895	-
$_{12}$C-H	1.076	-	-	-	-
$_{11}$C-$_{12}$C	1.387	1.386	1.386	1.386	1.370
$_{12}$C=$_{13}$C	1.386	1.377	1.383	1.382	
$_{5}$C=$_{7}$N	1.303	1.304	1.316	1.316	
$_{2}$N-H	-	-	-	-	0.86

3.2 Mulliken Atomic Charges

Mulliken population is a method used to determine atomic charge. Mulliken atomic charge for atoms in PIP, 4-FPIP, 4-ClPIP, and 4-BrPIP compounds were listed in table 2. It was found that all nitrogen atoms and halogen atoms in the compounds possess negative charge. Negative charge also possessed by carbon atoms in the aromatic ring. These negative charges indicate that the molecule can be adsorbed actively to iron metal surface through the negatively charged atoms. The negatively charged atoms were the possible sites of absorption to the metal surface.

3.3 Electronic Properties

Electronic properties provide informations about the tendency of inhibitor molecule to interract with metal surface. The electronic properties calculated were dipole moment (D), HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), HOMO/LUMO energy gap (E_{GAP}), ionization potential (I), electron affinity (A), electronegativity (χ), and global hardness (η). The values of each electronic properties on each compounds were listed in table 3.

From the calculated dipole moment values, it was found that 4-BrPIP molecule has the highest dipole moment (5.994 D). The compounds have similar value of E_{GAP} in the range of 9.1-9.4 eV which is in agreement with previous report for similar molecule using RHF level of theory [23]. HOMO energy indicates the easiness of electron donation from inhibitor molecule to LUMO of iron metal. Higher HOMO energy will results in the easier electron donation to iron metal. Higher HOMO energy will results in lower ionization potential.

LUMO energy is related to the easiness of electron 'back' donation from iron atom to inhibitor molecule. Lower LUMO energy will results in higher possibility for the 'back' donation to be occured and strenghtening the interaction between inhibitor molecule and the iron metal atom. Lower LUMO

energy will results in higher value of electron affinity. 4-BrPIP has the highest HOMO energy, lowest ionization potential, and lowest LUMO energy among the molecules studied in this paper. Therefore, 4-BrPIP has the lowest energy gap i.e. 9.098eV. The energy gap value decreasing with order: 4-FPIP > PIP > 4-ClPIP > 4-BrPIP. The lower energy gap value correlates with better inhibition activities, thus, based on HOMO-LUMO energy, 4-BrPIP will have the highest activity as inhibitor molecule.

Table 2. Mulliken atomic charge of atoms in PIP, 4-FPIP, 4-ClPIP, and 4-BrPIP molecule.

Atomic charge	PIP	4-FPIP	4-ClPIP	4-BrPIP
1C	-0.119	-0.357	-0.355	-0.359
2C	-0.244	-0.085	-0.111	-0.119
3C	-0.178	0.054	0.060	0.060
4C	0.194	0.011	-0.010	-0.081
5C	0.626	0.379	0.353	0.356
6N	-0.737	-0.245	-0.249	-0.249
7N	-0.651	-0.320	-0.317	-0.319
8C	0.800	0.217	-0.706	-0.170
9C	0.181	-0.213	-0.226	-0.213
10C	-0.039	0.608	-0.003	0.137
11C	-0.133	-0.221	-0.020	0.326
12C	0.151	0.026	0.471	-0.590
13C	-0.149	-0.391	0.053	0.320
14C	-0.144	-0.290	-0.275	-0.157
15C	-0.155	0.034	-0.182	0.361
25H	0.146	-	-	-
25F	-	-0.407	-	-
25Cl	-	-	-0.281	-
25Br	-	-	-	-0.025

Table 3. Electronic properties for PIP, 4-FPIP, 4-ClPIP, and 4-BrPIP molecule

Compound	(D)	E_{LUMO}	E_{HOMO}	ΔE	*I*(eV)	*A* (eV)	*X*(eV)	η(eV)
PIP	3.745	1.647	-7.627	9.274	7.627	-1.647	2.989	4.637
4-FPIP	5.486	1.576	-7.831	9.407	7.831	-1.576	3.128	4.704
4-ClPIP	5.856	1.540	-7.603	9.143	7.603	-1.540	3.032	4.572
4-BrPIP	5.994	1.519	-7.579	9.098	7.579	-1.519	3.030	4.549

Electronegativity (χ) is the ability of an atom to attract electron from other atom in a compound. The electronegativity of the inhibitor compounds are lower than iron atom in bulk phase with value around 7 eV [24,25]. Therefore, the transfer of electron from inhibitor molecules to iron atom can be occured. 4-BrPIP molecule has the second-lowest value of electronegativity (3.030 eV), while PIP molecule has the lowest value of electronegativity (2.989 eV). Lower value of electronegativity is interpreted as more reactive molecule toward metal surface among the molecule studied in this paper. PIP and 4-BrPIP are more reactive toward metal surface because of H and Br atom have higher tendency to donate electron than F and Cl atom due to its electronegativity. Global hardness (η) also can predict chemical reactivity and structural stability of an inhibitor molecule [24,25]. Lower global hardness indicates a more reactive inhibitor molecule toward iron atom, which results in better inhibition efficiency. 4-BrPIP molecule has lowest value of hardness (4.549 eV), thus having greatest reactivity among the compounds studied in this paper.

4. Conclusion

Optimized structure and electronic properties of 2-phenylimidazole[1,2α]pyridine (PIP), 2-(4-fluorophenyl)imidazole[1,2α]pyridine (4-FPIP), 2-(4-chlorophenyl)imidazole[1,2α]pyridine (4-ClPIP), 2-(4-bromophenyl)imidazole[1,2α]pyridine (4-BrPIP) have successfully obtained through computational calculation. The resulting molecular structures provide comparable values of bond

lengths and dihedral angles with previous experimental report. The calculated electronic properties conclude that 2-(4-bromophenyl)imidazole[1,2α]pyridine (4-BrPIP) has better potential as corrosion inhibitor compared to the other three compounds studied. This compound has largest dipole moment and highest HOMO energy, i.e. 5,994 D and -7,579 eV respectively. 2-(4-bromophenyl)-imidazole[1,2α]pyridine (4-BrPIP) also has lowest value of energy gap, ionization potential, electron affinity, electronegativity, and global hardness, i.e. 9.138 eV, 7.619 eV, -1.519 eV, 3.050 eV, and 4.569 eV respectively.

Acknowledgement
This research was supported by Pusat Penelitian dan Penerbitan, Lembaga Penelitian dan Pengabdian Kepada Masyarakat (LP2M) UIN Sunan Gunung Djati Bandung.

References

[1] S. Martinez 2002 Mater. *Chem. Phys*. 77 97.
[2] A Popova, M Christov, S Rachieva and E Sokolova 2004 *Corros. Sci.* 46 1333
[3] I B Obot, N O Obi-Egbedi and S A Umoren 2009 *Int. J. Electrochem. Sci.* 4 863
[4] R BuBar, M Nielinger and H J Baltruschat 2005 *J. Electroanal. Chem.* 578 259–271
[5] H Ashassi-Sorkhabi, M R Majidi and K Seyyedi 2004 *Appl. Surf. Sci.* 225 176–185
[6] K F Khaled and N Hackerman 2003 *Electrochim. Acta 48* 2715–2723
[7] S A M Refaey, F. Taha and A.M. Abd El-Malak 2004 *Appl. Surf. Sci.* 236 175–185
[8] D Wang, S Li, Y Ying, M Wang, H Xiao and Z Chen 1999 *Corros. Sci*. 41 1911
[9] M Housni, Y Kusumawati, S Farhat, N Jouini, A L Ivansyah, M A Martoprawiro and Th. Pauporté 2015 *ACS Appl. Mater. Interfaces* 7 1568-1577
[10] Y Kusumawati, J Massin, C Olivier, T Toupance, A L Ivansyah, M A Martoprawiro, B Prijamboedi, C L Radiman and T Pauporté 2017 *Journal of Photochemistry and Photobiology A : Chemistry* 341 69-77
[11] A L Ivansyah, M A Martoprawiro and Buchari 2017 *IOP Conf. Series: Journal of Physics: Conf. Series* 812 012070.
[12] C D D Sundari, M A Martoprawiro and A L Ivansyah 2017 *IOP Conf. Series: Journal of Physics: Conf. Series* 812 012068
[13] J Cruz, E Garcı´a-Ochoa and M Castro 2003 *J. Electrochem. Soc*. 150 26
[14] X F Liu, S J Huang and H C Gu 2002 *Int. J. Fatigue* 24 803-809
[15] R Subramanian and V Lakshminarayanan 2002 *Corros. Sci*. 44 535–554.
[16] X.R. Ye, X Q Xin, J J Zhu and Z L Xue 1998 *Appl. Surf. Sci*. 135 307–317.
[17] a). Alex A. Granovsky, Firefly version 8, http://classic.chem.msu.su/gran/firefly
b). M W Schmidt, K K Baldridge, J A Boatz, S T Elbert, M S Gordon, J H Jensen, S Koseki, N Matsunaga, K A Nguyen, S Su, T L Windus, M Dupuis, J A Montgomery 1993 *J.Comput.Chem*. 14 1347-1363
[18] Marcus D Hanwell, Donald E Curtis, David C Lonie, Tim Vandermeersch, Eva Zurek and Geoffrey R Hutchison 2012 *Journal of Cheminformatics* 4 17
[19] Chemcraft ver. 1.8. https://www.chemcraftprog.com
[20] R G Pearson 1988 *Inorg. Chem*. 27 734.
[21] S Martinez, Mater 2002 *Chem. Phys.* 77 97
[22] Barforoush, Naderi, Ghanbarpour, Tehrani, & Khavasi, Acta Crystallographic Section E: Structure Reports Online 67 (12), o3248-o3248
[23] G Bereket, E Hür and C Öğretir 2002 *J. Mol. Struct.* (Theochem) 578 79-88
[24] Abelev E, Sellberg J, Ramanarayanan TA and Bernasek SL 2010 *J Mater Sci* 44 6167
[25] Camila G. Dariva., Alexandre F. Galio 2014 InTech