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Ab Initio Study on Electronic Structure of Some Imidazole Derivatives and Its Correlation with Corrosion Inhibition Properties

C D D Sundari1,*, S Setiadji2, B W Nuryadin3, R Syafia2, A F Huda4 and A L Ivansyah5

1Department of Chemistry Education, UIN Sunan Gunung Djati Bandung, Jl. A.H. Nasution No.105 Bandung, West Java, 40614, Indonesia
2Department of Chemistry, Faculty of Science and Technology, UIN Sunan Gunung Djati Bandung, Jl. A.H. Nasution No.105 Bandung, West Java, 40614, Indonesia
3Department of Physics, Faculty of Science and Technology, UIN Sunan Gunung Djati Bandung, Jl. A.H. Nasution No.105 Bandung, West Java, 40614, Indonesia
4Department of Mathematics, Faculty of Science and Technology, UIN Sunan Gunung Djati Bandung, Jl. A.H. Nasution No.105 Bandung, West Java, 40614, Indonesia
5Master Program in Computational Science, Faculty of Mathematics and Natural Science, Institut Teknologi Bandung, Jl. Ganesha No. 10, Bandung, West Java, 40132, Indonesia

*cit@uinsgd.ac.id

Abstract. Imidazole and some of its derivatives have been known as a good candidate for corrosion inhibition application. In this study, ab initio calculation was carried out for several imidazole derivatives i.e. 2-phenylimidazole[1,2-α]pyridine, 6-methyl-2-phenylimidazole[1,2-α]pyridine, 6-methyl-2-(4-metoxyphenylimidazole)[1,2-α]pyridine, and 6-methyl-2-(4-chlorophenylimidazole)[1,2α]pyridine, in order to investigate their electronic properties as well as its correlation with their corrosion inhibition properties. Calculations were performed using Firefly software package with RHF method and 6-31G(d,p) basis set. Based on calculation results and analysis, it was found that 6-methyl-2-(4-metoxyphenylimidazole)[1,2α]pyridine compound has better potential as corrosion inhibitor than the rest of the compounds due to its small HOMO-LUMO energy gap, low ionization potential, low electron affinity, low electronegativity, and low global hardness i.e. 10.184 eV, 7.199 eV, -2.985 eV, 2.107 eV and 5.092 eV respectively. This compound also has the highest global softness (0.098 eV), while the greatest value of the dipole moment was owned by 6-methyl-2-(4-chlorophenylimidazole)[1,2α]pyridine with value of 6.125 Debye due to the existence of Cl atom that has larger polarity than the other substituents.

1. Introduction
Corrosion is degradation of metal surface quality due to oxidation-reduction reaction with the surrounding environment, especially corrosive media. If not promptly handled, corrosion will results in substantial material loss. The utilization of corrosion inhibitor is an effective and economic method
to protect metal surface from corrosion by decreasing corrosion rate [1]. Organic corrosion inhibitor have more advantageous properties i.e environment-friendly and low toxicity. Various types of organic compounds have been widely used as corrosion inhibitors. One of the factors influencing the corrosion inhibition efficiency of an organic compound is the presence of heteroatom such as O, N, S and P on the molecule. The presence of an appropriate functional group will assist the formation of complexes between organic compounds and metal surfaces or assist the adsorption of inhibitor molecule on the metal surface. On the metal surface, organic inhibitor molecule forms a coating that prevents metal surfaces from contact with corrosive media [2].

Imidazole compound and some of its derivatives have been used as corrosion inhibitors [3,4,5]. One of the imidazole derivative i.e. 7-methyl-2-phenylimidazole[1,2-α]pyridine, has shown a good efficiency as a corrosion inhibitor and acts as a cathodic inhibitor [5]. The efficiency of corrosion inhibition of this compound is influenced by inhibitor concentration and temperature [5]. Other imidazole derivatives such as 4-methyl-1-phenyl imidazole, 4-methyl-1-(p-tolyl) imidazole, and 1-methyl-2-mercapto imidazole have also been found to be an efficient corrosion inhibitor [6-7]. Computational calculation of imidazole derivatives can help assessing (design, calculate, and analyze) potential corrosion inhibitor [8-10], which gives information complementing laboratory-scale experimental studies. There are several level of theories which is used in molecular modeling, such as DFT, ONIOM, Semiempiric Quantum, Molecular Dynamics, and Molecular Mechanics. Among them, semiempiric quantum method using PM3 and ONIOM are one of the method that has good cost-performance ratio which has been used by researcher in molecular modeling [11,12]. However, DFT theory level is the best level of theory with high accuracy for molecular modeling, especially for corrosion inhibitor application.

In this research, molecular structure and electronic properties of several imidazole derivatives i.e. 2-phenylimidazole[1,2-α]pyridine, 6-methyl-2-phenylimidazole[1,2-α]pyridine, 6-methyl-2-(4-methoxy-phenylimidazole)[1,2α]pyridine and 6-methyl-2-(4-chlorophenylimidazole)[1,2α]pyridine have been calculated computationally with ab initio method [10,13,14]. The results of the calculation with this method provide comparable results in accordance with the experimental results.

2. Computational Details
All calculations of the compounds, i.e. 2-phenylimidazole[1,2-α]pyridine, 6-methyl-2-phenylimidazole [1,2-α]pyridine, 6-methyl-2-(4-methoxyphenylimidazole)[1,2α]pyridine and 6-metil-2-(4-chlorophenylimidazole)[1,2α]pyridine were carried out using Firefly 8.2.0 [15] software package. The initial geometry of these four molecules was constructed using Avogadro 1.0 [16] software package and output of the calculations were visualized using Chemcraft 1.8 [17]. All ab initio calculations were performed at Restricted-Hartree Fock (RHF) level of theory with 6-31G(d,p) basis set for all atoms. Two dimensional structure of the compounds calculated in this research are presented in figure 1.

![Figure 1. Structure of: (a) 2-phenylimidazole[1,2-α]pyridine, (b) 6-methyl-2-phenylimidazole[1,2-α]pyridine, (c) 6-methyl-2-(4-methoxyphenylimidazole)[1,2-α]pyridine and (d) 6-metil-2-(4-chlorophenylimidazole)[1,2-α]pyridine.](image-url)
3. Results and Discussion

3.1. Optimized Structure, Atomic Charge and Electron Density Distribution in Orbitals

The optimized structure calculations were performed using RHF method with 6-31G(d,p) basis set in the gas phase. The result of structural optimization as well as bond length between atoms can be seen in figure 2. All optimized structures have planar shape with dihedral angle of 0° and 180° between atoms in phenyl and imidazole ring.

![Optimized Structure](image)

Figure 2 Optimized structure of: (a) 2-phenylimidazole[1,2-α]pyridine, (b) 6-methyl-2-phenylimidazole[1,2-α]pyridine, (c) 6-methyl-2-(4-methoxyphenylimidazole)[1,2-α]pyridine and (d) 6-methyl-2-(4-chlorophenylimidazole)[1,2-α]pyridine.

Mulliken atomic charge is used to describe the electron density of each atom in the molecule. The negative sign for the atomic charge shows a high electron density, whereas a positive sign indicates that the atom lacks electrons. The negative charge of N and O atoms and the most negative carbon atom charge on the ring structure is the active part for the adsorption by the metal surface. Heteroatom is the active site that contributes to adsorption with metal atoms through electron donor-acceptor mechanism. The more negative the atomic charge will allow better adsorption to the metal surface. Table 1 lists the Mulliken atomic charge of atoms (except hydrogen atom) in the imidazole derivative molecules. Nitrogen and oxygen atom in each molecules possess the most negative charge.

| Atomic charge | (A) | (B) | (C) | (D) |
|---------------|-----|-----|-----|-----|
| C₁            | -0.119 | -0.112 | -0.112 | -0.111 |
| C₂            | -0.244 | -0.099 | -0.100 | -0.099 |
| C₃            | -0.178 | -0.177 | -0.178 | -0.177 |
| C₄            | 0.194  | 0.178  | -0.178 | 0.178  |
| C₅            | 0.626  | 0.622  | 0.623  | 0.624  |
| N₁            | -0.737 | -0.741 | -0.740 | -0.742 |
| N₂            | -0.656 | -0.656 | -0.661 | -0.657 |
| C₆            | 0.066  | 0.068  | 0.062  | 0.071  |
| C₇            | 0.181  | 0.176  | 0.187  | 0.177  |
| C₈            | -0.039 | -0.037 | -0.069 | -0.044 |
| C₉            | -0.133 | -0.134 | -0.114 | -0.125 |
| C₁₀           | -0.151 | -0.150 | -0.191 | -0.117 |
| C₁₁           | -0.149 | -0.150 | 0.412  | -0.166 |
| C₁₂           | -0.144 | -0.145 | -0.131 | -0.137 |
Electron density distribution in HOMO and LUMO orbitals of the molecules are shown in figure 3. The presence of electron donor and electron withdrawing group affects the electron density in the HOMO and LUMO orbital of the molecules. Electron in HOMO orbitals is distributed evenly in the molecules, excluding the methyl group, indicating sites with high tendency to donate electrons. Metoxy substituent in 6-methyl-2-(4-metoxophenylimidazole)[1,2-α]pyridine effectively push electrons to nitrogen atom in imidazole as shown in electron distribution of LUMO orbital of this compound.

3.2. Electronic Properties

Electronic parameters give information about the ability of the inhibitor molecules to interact with metal surface. Electronic properties calculated were HOMO energy ($E_{\text{HOMO}}$), LUMO energy ($E_{\text{LUMO}}$), energy gap ($E_{\text{GAP}}$), ionization potential (I), electron affinity (A), electronegativity ($\chi$), chemical potential ($\mu$), global hardness ($\eta$), global softness (S), dipole moment (DM), and electron transfer fraction ($\Delta N$) [1,10,14,18]. These properties are presented in table 2.

Inhibition efficiency is related with the value of HOMO energy ($E_{\text{HOMO}}$), LUMO energy ($E_{\text{LUMO}}$), and energy gap ($E_{\text{GAP}}$). Higher HOMO energy indicates higher ability of the molecule to donate electron. Energy gap (band gap) is the difference between LUMO and HOMO energy ($E_{\text{GAP}} = E_{\text{LUMO}} - E_{\text{HOMO}}$).
Electron transfer fraction ($\Delta N$) represents the ease of a molecule to donate electron. The electronegativity of all four inhibitor compounds are lower than iron (Fe) atom in bulk form ($\approx 7$ eV) [1,2] supporting the transfer of electron from inhibitor molecule to iron atom. 6-methyl-2-(4-methoxyphenylimidazole)[1,2-\(\alpha\)]pyridine has lowest value of electronegativity (2.107 eV) and highest chemical potential (2.107 eV) and highest chemical potential (2.107 eV), making it more reactive toward metal surface. Global hardness ($\eta$) and softness ($S$) also can predict chemical reactivity and structural stability of an inhibitor molecule [1,2]. Higher global softness (smaller global hardness) indicates a more reactive inhibitor molecule.

According to DFT-Koopmans theorem [1,2], the ionization potential (I) is correlated with the negative HOMO energy ($I = -E_{\text{HOMO}}$), and negative LUMO energy is correlated with the electron affinity ($A = -E_{\text{LUMO}}$). Electronegativity and chemical potential of inhibitor molecule were calculated using ionization potential (I) and electron affinity (A). Electronegativity ($\chi$) is the ability of an atom to attract electron from other atom in a compound. Electronegativity is correlated with the average value of I and A ($\chi = (I + A)/2$) and chemical potential ($\mu$) is correlated with negative electronegativity ($\mu = -\chi$). The electronegativity of all four inhibitor compounds are lower than iron (Fe) atom in bulk form ($\approx 7$ eV) [1,2] supporting the transfer of electron from inhibitor molecule to iron atom. 6-methyl-2-(4-methoxyphenylimidazole)[1,2-\(\alpha\)]pyridine has lowest value of electronegativity (2.107 eV) and highest chemical potential (2.107 eV) and highest chemical potential (2.107 eV), making it more reactive toward metal surface. Global hardness ($\eta$) and softness ($S$) also can predict chemical reactivity and structural stability of an inhibitor molecule [1,2]. Higher global softness (smaller global hardness) indicates a more reactive inhibitor molecule, which results in better inhibition efficiency. Global hardness can be expressed from HOMO and LUMO energy by equation: $\eta = (I - A)/2$. 6-methyl-2-(4-methoxyphenylimidazole)[1,2-\(\alpha\)]pyridine has lowest value of hardness (5.092 eV), thus having greatest reactivity among the compounds studied in this paper.

The electron transfer fraction ($\Delta N$) represents the ease of a molecule to donate electron. The value of this parameter is equal to the ratio of the electronegativity difference to the sum of hardness between inhibitor compound with metal atom in bulk phase ($\Delta N = (\eta_{\text{Fe}+} - \eta_{\text{Fe}})/2(\eta_{\text{Fe}+} + \eta_{\text{Fe}}) \approx 0$) [1,2,5]. Inhibition efficiency of inhibitor molecule increases as the donation of electron to the metal surface getting easier. Large $\Delta N$ value indicates a good tendency to interact with metal atoms. 6-methyl-2-(4-methoxyphenylimidazole)[1,2-\(\alpha\)]pyridine compound has the greatest $\Delta N$ value (0.481 eV) compared to the other compounds.

### Table 2

| Compound | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $\Delta N$ (eV) | Dipole Moment (D) | Softness (S) (eV) | Global Softness ($S$) (eV) | Global Hardness ($\mu$) (eV) | Global Chemical Potential ($\chi$) (eV) | Global Electronegativity ($\chi$) (eV) |
|----------|-----------------------|-----------------------|----------------|-------------------|-------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| (A)      | -7.574                | 2.774                 | 0.481          | 6.125             | 2.651             | 2.107                    | 2.400                    | 2.400                    | 5.174                    |
| (B)      | -7.506                | 2.865                 | 0.450          | 6.075             | 2.985             | 2.107                    | 2.321                    | 2.321                    | 5.189                    |
| (C)      | -7.199                | 2.985                 | 0.481          | 6.075             | 2.985             | 2.107                    | 2.107                    | 2.107                    | 5.092                    |
| (D)      | -7.688                | 2.651                 | 0.433          | 6.125             | 2.651             | 2.107                    | 2.519                    | 2.519                    | 5.170                    |

Dipole moment can also predicts inhibition efficiency related to the adsorption capability of inhibitor molecule. The electrostatic interaction between the negatively charged center of inhibitor molecule and the positively charged metal surface is a dipole interaction which illustrates physisorption. The positive sign of the dipole moment characterizes that the molecule can be adsorbed physically by metal surface. Increasing dipole moment correlates to improved inhibition efficiency. This is related to the better interaction of physisorption. Table 2 shows that the four compounds are polar, but 6-methyl-2-(4-chlorophenylimidazole)[1,2-\(\alpha\)]pyridine has the largest dipole moment (6.125 Debye) compared to other compounds due to highly electronegative Cl substituent.

4. **Conclusion**

Computational calculations and studies have been performed to investigate structure and electronic properties from four imidazole derivative compounds, i.e. 2-phenylimidazole [1,2-\(\alpha\)]pyridine, 6-methyl-2-phenylimidazole[1,2-\(\alpha\)]pyridine, 6-methyl-2-(4-methoxyphenylimidazole)[1,2-\(\alpha\)]pyridine and 6-methyl-2-(4-chlorophenylimidazole)[1,2-\(\alpha\)]pyridine. The calculation results conclude that 6-
methyl-2-(4-metoxyphenylimidazole)[1,2-α]pyridine has better electronic properties than the other three compounds. This is indicated by the smallest value of energy gap (E_{\text{GAP}}), lowest electronegativity (\chi), largest HOMO (E_{\text{HOMO}}) energy, lowest ionization potential (I), highest chemical potential (\mu), lowest hardness (\eta), and highest electron transfer fraction (\Delta N). In addition, the calculations predict that the 6-methyl-2-(4-chlorophenylimidazole)[1,2-α]pyridine has the greatest dipole moment, making it more polar than the other three compounds presented.

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