

Quantum Chemical Calculations for Corrosion Inhibition of Pyrimidine Derivatives

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Abstract: The inhibition properties of compounds have been correlated with frontier orbital energy of highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), and energy gap ($\Delta E_{\text{LUMO-HOMO}}$). There is a good correlation between the speed of corrosion and E_{HOMO} that is often associated with the electron donating ability of the molecule. The literature shows that the adsorption of the molecule on the metal surface can occur on the basis of donor–acceptor interactions between the lone pairs on hetero atoms or π electrons of the molecule and the empty d orbital of the metal atom. In the present work, pyrimidine derivatives have been investigated as corrosion inhibitors for iron using density functional theory.

Keywords: Pyrimidine, Corrosion, Quantum chemical calculation

Introduction

The deterioration of materials due to corrosion causes economic loss. A wide variety of research is conducted to prevent this harmful process. One of the excellent methods to protect materials against corrosion is use of heterocyclic compounds containing π -electrons (Elmors, at al., 1999). The physicochemical parameters of the molecules are important because they determine adsorption on the metal surface. Most effective inhibitor molecules behave as both electron donor and electron acceptor (Ikpi, at al., 2017). When using heterocyclic compounds for corrosion inhibition are sharing the lone pairs on hetero atoms or π electrons to over metal surface and the molecule is adsorb on the metal surface (Lagrenée, at al., 2002).

The quantum chemical calculations have been widely used to the reactivity of organic compounds for corrosion inhibition (Khalil, 2003). The inhibitor activities are involved molecular geometry and orbitals of the organic compounds and correlated with frontier orbital energy. The highest occupied molecular orbital energy (E_{HOMO}) is associated with the electron donating ability of the molecule. There is a good correlation between the speed of corrosion and E_{HOMO} . The adsorption of the molecule on the metal surface can occur on the basis of donor–acceptor interactions between the lone pairs on hetero atoms or π electrons (Caliskan, at al., 2012). The high E_{HOMO} value has a molecule tendency to give electrons, while a low E_{LUMO} value indicates the ability of the molecule to accept electrons. The difference between E_{LUMO} and E_{HOMO} energies is called energy gap. Larger values of the energy gap will provide low reactivity to a chemical interaction and inhibition efficiency. But the lower values of the ΔE will render good reactivity to a chemical interaction and inhibition efficiency (Karzazi, at al., 2014).

The ionization potential (I) and electron affinity (A) of the inhibitor molecule and E_{HOMO} and E_{LUMO} are related to each other. The absolute electronegativity (χ) and the global hardness (η) depending on the ionization potential and electron affinity of the inhibitor molecules, the following can be given (1) (Karzazi, at al., 2014).

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$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\bar{r})} \quad \eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\bar{r})} = \left(\frac{\partial \mu}{\partial N}\right)_{v(\bar{r})} \quad (1)$$

The chemical softness (S) is a chemical descriptor measuring the molecular stability and reactivity. The relation between chemical softness (S) and chemical hardness can be given as follows (2) (Karzazi, at al., 2014).

$$S = \frac{1}{\eta} \quad (2)$$

The global electrophilicity index (ω) is a measure of energy lowering due to maximal electron flow between donor and acceptor. It can be given as a function of the dipole moment and the chemical hardness as follows (3) (Karzazi, at al., 2014).

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

The global electrophilicity index measures the tendency of molecules to accept electrons. A molecule with a high ω value has an electrophile and with a low ω value has a nucleophilic character.

The transferred electrons fraction index (ΔN) measures the stabilization in energy when the system acquires an additional electronic charge from the environment. Thus the fraction of electrons transferred from the inhibitor to metallic surface (4) (Chattaraj, at al., 2006).

$$\Delta N = \frac{\chi_{F_e} - \chi_{inh}}{2(\eta_{F_e} + \eta_{inh})} \quad (4)$$

According to the simple charge-transfer model there are occurring governing the interaction between the inhibitor molecule and the metal surface (5) (Ramírez-Ramírez, at al., 2010).

$$\Delta E_{back\ donation} = -\frac{\eta}{4} \quad (5)$$

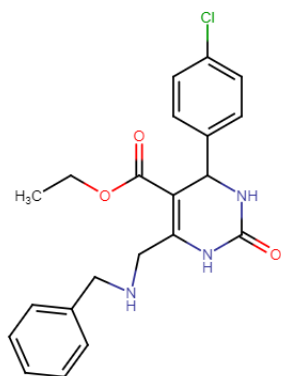
The $\Delta E_{back\ donation}$ implies that when $\eta > 0$ and $\Delta E_{back\ donation} < 0$ the charge-transfer to a molecule, followed by a back donation from the molecule, is energetically favored.

Method of Calculation

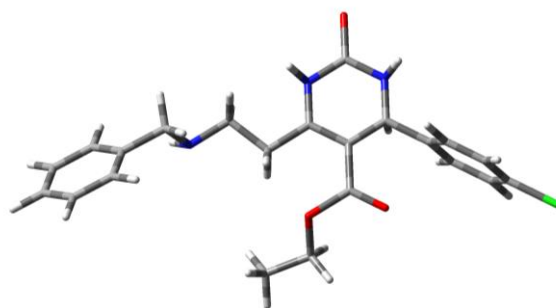
The quantum chemical parameters of the earlier pyrimidine derivatives (Fatima, at al., 2018) were calculated using DFT based on Beck's three parameter exchange functional and Lee–Yang–Parr nonlocal correlation functional (B3LYP) and the 6-31G (d, p) orbital basis sets in Gaussian09 program (Becke,1993; Lee, at al., 1988; Frisch, at al., 2009).

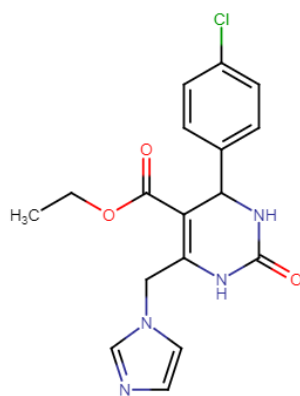
Results and Discussion

The quantum chemical calculations of the all molecules have been performed using DFT based on Beck's three parameter exchange functional and Lee–Yang–Parr nonlocal correlation functional (B3LYP) and the 6-31G (d, p) orbital basis sets in Gaussian09 program (Fig.1). This method has been widely implemented to study the relationship between corrosion inhibition efficiency of the molecules and their electronic properties (Young, 2001).

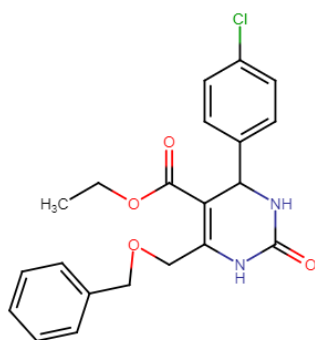
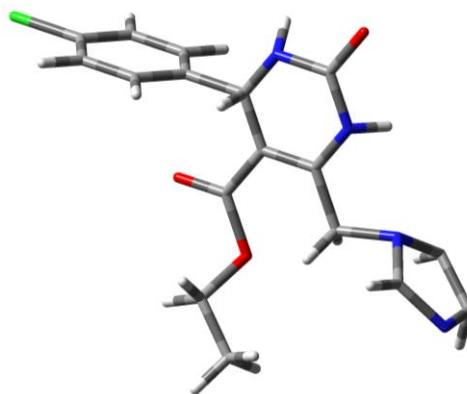


Compound. 1_(Fatima, at al., 2018)





Compound. 2_(Fatima, at al., 2018)



Compound. 3_(Fatima, at al., 2018)

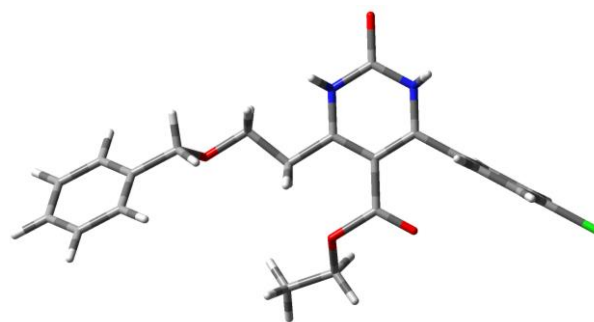


Figure 1. Names, molecular and optimized structures of the compounds

The quantum chemical parameters of all compounds such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap (ΔE), dipole moment (μ), ionization potential (I), electron affinity (A), absolute electronegativity (χ), chemical hardness (η), global electrophilicity index (ω), chemical softness (S), fraction of electrons transferred (ΔN) and back donation energy ($\Delta E_{\text{back donation}}$) were calculated (Table 1).

Table 1. Calculated quantum chemical parameters of the studied molecules

Compounds	1	2	3
E_{HOMO} (eV)	-5.9053	-6.2560	-6.0301
E_{LUMO} (eV)	-1.9619	-2.4420	-2.0686
Ionization potential: I (eV)	5.9053	6.2560	6.0301
Electron affinity: A (eV)	1.9619	2.4420	2.0686
Electronegativity: χ (eV)	3.9336	4.3490	4.0894
Chemical hardness: η (eV)	3.9434	3.8140	3.9615
Chemical softness: S	0.2536	0.2622	0.2524
Dipole moment: μ (debye)	4.3615	4.6606	3.7917
Electrophilicity index: (ω)	2.4119	2.8476	1.8148
Transferred electrons fraction: (ΔN)	0.3888	0.3475	0.3674
Energy gap: $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ (eV)	3.9434	3.8140	3.9615
$\Delta E_{\text{back donation}}$	-0.9858	-0.9535	-0.9904

According to the frontier molecular orbital theory of the chemical reactivity is depends interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency towards the donation of electron by a molecule. Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on metal and therefore better inhibition efficiency. E_{LUMO} indicates the ability of the molecule to accept electrons. The binding ability of the inhibitor to the metal surface increases with increasing of the HOMO and decreasing of the LUMO energy values. Frontier molecular orbital diagrams of 1, 2 and 3 are represented in fig. 2.

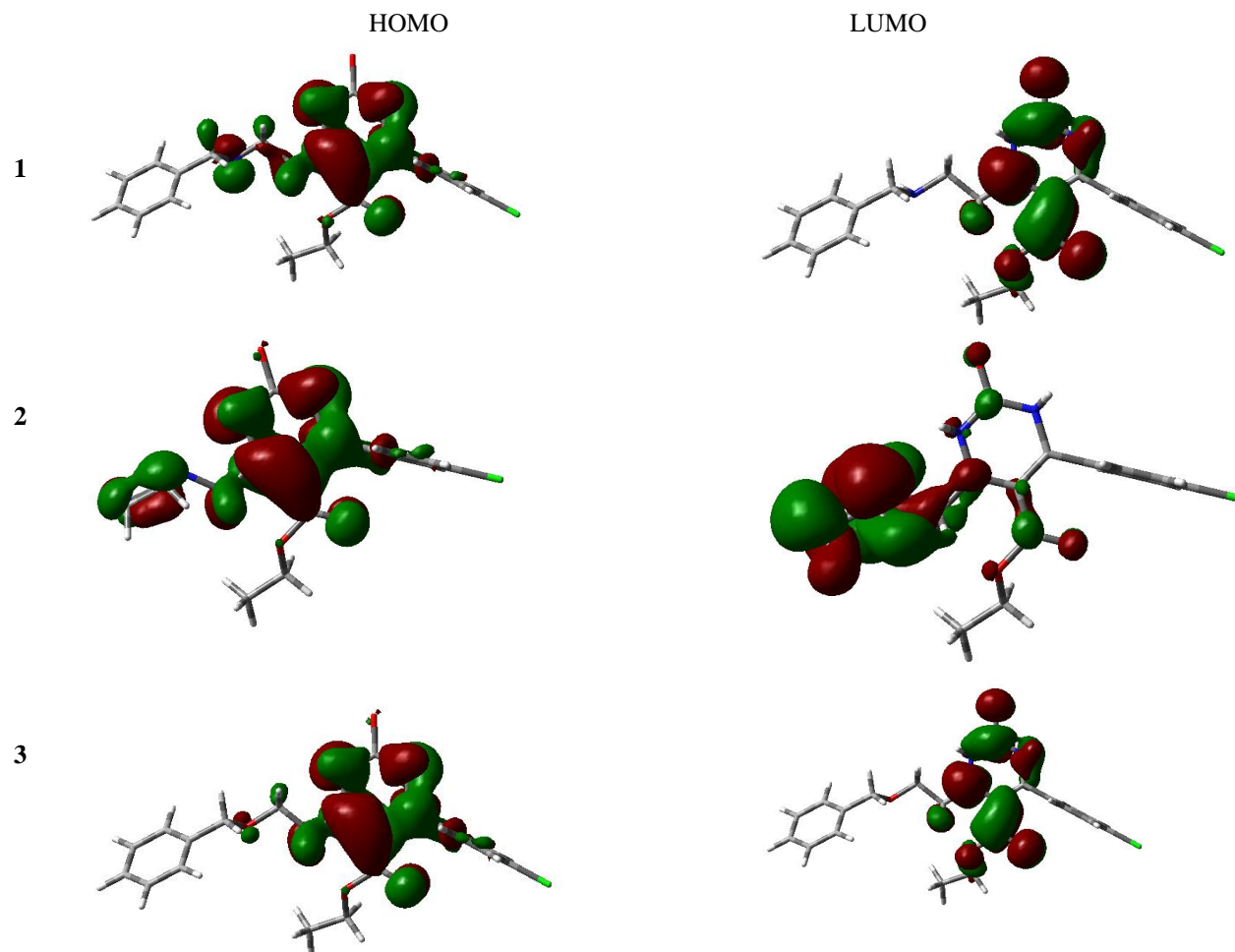


Figure 2. Frontier molecular orbital diagrams of 1, 2 and 3

E_{HOMO} for the three compounds follows the order; $1 > 3 > 2$ which implies that 1 has the highest tendency to donate electrons (Table 1). High value of E_{HOMO} is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy.

The ionization energy is one of a fundamental descriptor the chemical reactivity of molecules. High ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of the molecules (Karzazi, at al., 2014). The compound 1 has the lowest ionization energy when compared with other compounds. This indicates that 1 has a high inhibitory effect.

The electron transferred (ΔN) and back-donation ($\Delta E_{\text{back-donation}}$) were also calculated (table 1). If $\Delta N < 3.6$, the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface (Karzazi, at al., 2014). The highest fraction of electrons transferred is associated with the best inhibitor.

The calculated $\Delta E_{\text{back donation}}$ values for the inhibitors reveal that back donation is favored for the molecule 1 which is the best inhibitor (table 1).

The molecular electrostatic potential (MEP) provides information about reactive sites for electrophilic and nucleophilic attack. In order to predict reactive sites for electrophilic and nucleophilic attack in all molecules, the MEP maps were also fixed in figure 3. The electrostatic potential on the surfaces have been represented by colors. The blue regions of MEP maps shows electrophilic, while the red areas shows nucleophilic reactivity.

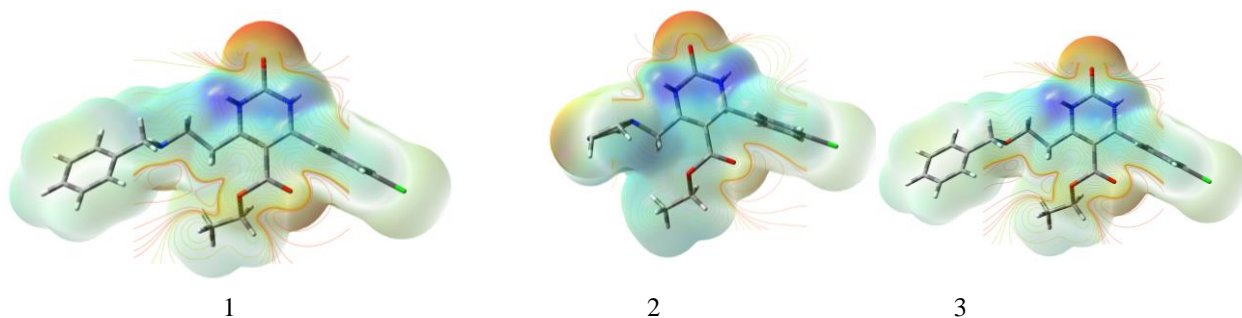


Figure 3. The molecular electrostatic potentials (MEPs)

Conclusion

The pyrimidine derivatives were investigated as corrosion inhibitors using density functional theory (DFT) at B3LYP/6-31G(d,p) level. From the results, it can be concluded that the compound 1 is good inhibitors for the corrosion.

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