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Research Article

Calculation of usability as anti-corrosion of pyrimidine-type bases by density functional theory

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ABSTRACT

Corrosion of metals is an important problem in many industries. This problem can be reduced by coating the metal surface. With this application, the metal can be isolated from the corrosive environment. Surface coating materials may be inorganic compounds as well as compounds of organic origin. In the case of organic compounds, these compounds are selected from groups rich in functional groups, containing free electron pairs and/or π electrons. In this study, pyrimidine derivatives were selected which is synthesized Robins et al. These compounds are very rich in functional group, free electron pairs and π electrons. To calculate the anticorrosive effects of the compounds theoretically, quantum chemical calculations were performed with the Gaussian09W software package using the density functional theory method (DFT) of all compounds, the 6-31G (d, p) base set and B3LYP functions. The quantum chemical computations showed that the studied compound was adsorbed differently on the metal surface all depend to the nature of the molecular structure.

Keywords: Pyrimidine-type bases, density functional theory, anti-corrosion, chemical calculation.

Yoğunluk fonksiyonel teorisi ile pirimidin tipi bazların korozyon önleyici olarak kullanılabilirliğinin hesaplanması

ÖZ

Metallerin korozyonu birçok endüstride ciddi bir sorundur. Metal yüzey kaplanarak bu sorun azaltılabilir. Bu uygulama ile metal, korozif ortamdan izole edilebilir. Korozyon önleyici, yüzey kaplama malzemeleri inorganik bileşikler olabileceği gibi organik kökenli bileşikler de olabilir. Organik bileşikler söz konusu olduğunda, bu bileşikler, serbest elektron çiftleri ve/veya π elektronları içeren fonksiyonel gruplar açısından zengin gruplardan seçilir. Bu çalışmada, antikorozif özelliklerini incelemek üzere Robins ve ark.'nın sentezlediği pirimidin türevleri seçildi. Bu bileşikler fonksiyonel grup, serbest elektron çiftleri ve π elektronları bakımından çok zengindir. Bileşiklerin antikorozif etkilerini teorik olarak hesaplamak için tüm bileşikler için yoğunluk fonksiyonel teorisi (DFT) yöntemi, 6-31G (d, p) baz seti ve B3LYP fonksiyonları kullanılarak Gaussian09W yazılım paketi ile kuantum kimyasal hesaplamaları yapıldı. Hesaplamalar, incelenen bileşiğin, moleküler yapının doğasına bağlı olarak metal yüzeyinde farklı şekilde adsorbe edildiğini gösterdi.

Anahtar Kelimeler: Pirimidin tipi bazlar, yoğunluk fonksiyonel teorisi, korozyon önleyici, kimyasal hesaplama.

1. INTRODUCTION

Acid solutions, which are widely used in industrial production, especially in cleaning processes, cause significant mass losses on the surface. These mass losses are due to corrosion on the metal surface. Many techniques have been developed to prevent corrosion occurring on the surface. One of these techniques is the use of organic compounds as corrosion inhibitors.

Organic compounds containing aromatic ring, heteroatom and π electrons show high inhibition property. Due to the high nucleophilic character of sulfur, it adheres to the methal surface more easily than oxygen and nitrogen atoms. Accordingly, the inhibition effect of heteroatoms will be O < N < S. [1] If the compounds containing heteroatoms also including π-electrons, further increasing the adsorption.

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It is desirable that the compounds used for corrosion preventive purposes are not harmful to nature. Therefore, pyrimidine derivatives are of great interest. Pyrimidine derivatives exhibit wide biochemical effects due to the activity of aromatic ring system, N atoms and π electrons. Due to these properties, pyrimidine compounds are promising for corrosion inhibition.

Many different experimental methods are used for corrosion inhibition. These are often very costly methods. They also fail to explain the inhibition mechanism of corrosion. For this reason, computational methods have recently been used frequently as an alternative to experimental methods. The quantum chemical calculation method is one of these computational methods. With this method, the working cost and time are reduced and the mechanism can be explained.

The inhibition effect is mostly connected to the electronic structure of the compounds. In the case of using organic compounds as inhibitors, the selected molecules must be able to donate electrons to the empty d-orbital of the metal and also be suitable to form anti-feedback bonds. Various methods have been developed to elucidate the electronic structures of compounds. One of these methods is the quantum chemical calculation method. In this study, the Gaussian09.6[2] package program was used which is one of the programs that can best use the quantum chemical calculation method. According to the frontier orbital theory, the reaction is due to an interaction between the Highest Molecular Orbital (HOMO) and Lowest Occupied Molecular Orbital (LUMO) boundary orbits of the compounds.

Therefore, correct interpretation of these energy levels is important to understand the inhibition effect. To understand the mechanism, it must be calculated in the energy gap (ΔE). The energy gap equals the difference between ELUMO and EHOMO energies. Low values of ΔE will provide perfect inhibition effect.

In order to determine the ability of the molecule to prevent corrosion that may occur on the metal surface, the absolute I, A, S, ω, ΔN and ΔEback-donation properties must be calculated. In this study, all these calculations were carried out according to Shojaie et al.[3] using Gaussian09.

2. MATERIALS AND METHODS

In this work, Gaussian package program was used for the quantum chemical calculations by density functional theory (DFT) at the B3LYP / 6-31G (d, p) level. With this program, many calculations that can be made with the quantum mechanical method can be done easily. These calculations allow us to predict the molecular properties, molecular structures, vibrational frequencies and reactions of the compounds. It is possible to calculate the optimum geometry, minimum energy, bond lengths, bond angles and dihedral angles for a compound.

As the geometric optimization calculations of large molecules are made with high level methods, they are very time consuming processes. Large molecules can have a large number of conformers whose global minimum and energies make it difficult to find local minimums as low as fairly large molecules can have. There are many special methods for conformational scanning whose aim is to find the low energy conformer. Due to the large number of conformers in question, energy calculations in conformational scanning with large molecules are usually made by molecular mechanics. The aim of this work is to determine the effectiveness of pyrimidine compounds with various bonded functional groups as corrosion inhibitors. For this purpose, quantum chemical parameters such as HOMO, LUMO, MEP, ΔE, the ionization potential, the electron affinity, chemical hardness and softness, general electrophilic index, transmitted electron fraction index and recovery (ΔEback-donation) were calculated.

3. RESULTS AND DISCUSSION

The geometric optimizations and quantum chemical parameters used to determine their corrosion inhibition potential of previously synthesized pyrimidine compounds[4] (Figure 1) has been studied by DFT calculations.

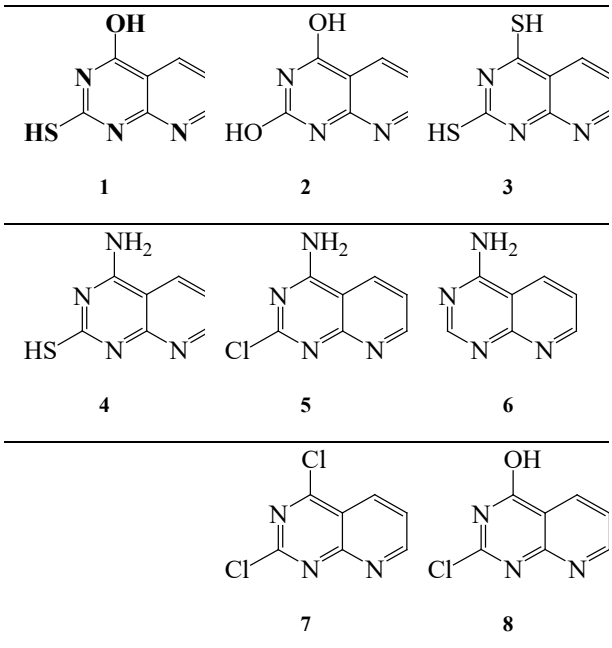

Figure 1. Molecular structures and schematic representation of pyrimidine derivatives

Theoretical calculations led to the development of experimental work. With theoretical calculations, corrosion activity parameters of the analyzed molecules against metal atoms can be calculated. Theoretical

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calculations have demonstrated that the molecule's filled highest energy orbital and empty lowest energy orbital values are the most important parameters in estimating the corrosion inhibition activity of the molecules against metal atoms. It can be found that molecules for which quantum chemical calculations are made are active molecules with parameters like EHOMO, ELUMO, ΔE, χ, μ, η, ω, σ. [5,6]

$$\mu = -\chi = \left(\frac{\partial E}{\partial N}\right)_{\vartheta(r)} \quad (1)$$

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

The I, A, χ, σ, η values of the studied molecules are obtained by EHOMO and ELUMO with the following equations are obtained:

$$\chi = -\mu = \left(\frac{-E_{HOMO}-E_{LUMO}}{2}\right) = \left(\frac{I+A}{2}\right) \quad (3)$$

$$\chi = -\mu = \left(\frac{-E_{HOMO}-E_{LUMO}}{2}\right) = \left(\frac{I+A}{2}\right) \quad (4)$$

σ is a chemical illustrator that surveys molecular stability and reactivity. σ is defined as the reverse of η.

$$\sigma = \frac{1}{\eta} \quad (5)$$

The ω is a survey of the energy drop because of the maximum electron run between donor and acceptor. It can be represented as a function of χ and η as shown in Eq. (6).

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi 2}{2\eta} \quad (6)$$

The ω surveys the ability of molecules to receive electrons. As the ω value of a molecule increases, its electrophilic character increases, and as it decreases, its nucleophilic character increases.

The electronegativity value of molecules is a parameter that helps to compare the reactivity of molecules. The value of this parameter is given to estimate the electron transfer between metal and inhibitor. The molecule with a high electronegativity value hardly gives any valence electrons to this molecule. Because these electrons are attracted to the nucleus more than other molecules. According to Sanderson's electronegativity equation[7], we calculate the value of the electrons transferred from the anti-corrosion molecule with the following equation.

$$\Delta N = \frac{\chi_M - \chi_{inh}}{2(\eta_M + \eta_{inh})} \quad (7)$$

Here χM and χinh are the electronegativity value of the metal and the inhibitor molecule, respectively. ηM and ηinh are the chemical hardness of the metal and the inhibitor molecule, respectively.

According to the simple charge transfer model, the electron donation and recovery process can be expressed as an electronic donation back process between the inhibitor molecule and the metal surface.

$$\Delta E_{back\ donation} = -\frac{\eta}{4} \quad (8)$$

The ΔEback donation implies that When η > 0 and ΔEback donation <0 the charge transfer to a molecule, followed by a back donation from the molecule, is energetically favored.

Fully geometric optimizations of all molecules, HOMO-LUMO diagrams, molecular electrostatic potential maps (MEPs) and corrosion inhibition parameters were calculated with DFT and B3LYP (d, p) base set in Gaussian09 program (Figure 2 and Table 1). It has been determined in some studies that this calculation method, which is carried out theoretically, is used to examine the relationship between corrosion inhibition efficiency and electronic properties of molecules.

MEPs that provide information about the molecular distribution of electrons are represented by different colors. In Figure 1, the negative (red) areas of the MEPs are associated with electrophilic reactivity and positive (blue) areas with nucleophilic reactivity. Electrostatic potential increases during red> orange> yellow> green> blue. The highest potential is on oxygen atoms.

The chemical reactivity properties of the inhibitor molecule depend on the interaction between HOMO and LUMO orbitals. The energy level of HOMO is defined as the skill of a molecule to donate electrons. Therefore, the molecule with a higher EHOMO value shows a better tendency to electron donation and increases the adsorption on the metal. Therefore, it provides better inhibition efficiency. The LUMO energy level is considered the ability of the molecule to accept electrons. A low LUMO energy level indicates that the molecule can gain electrons more easily. The high HOMO-low LUMO values of the inhibitor increase its adhesion to the metal surface.

One of the important parameters determining the reactivity of the inhibitor is the energy gap value (ΔEgap). The ΔEgap value of the inhibitor indicates its ability to bind to the metal surface. The value of ΔEgap is calculated from the difference between the LUMO energy and the HOMO energy. The low energy gap value (ΔEgap) means that the inhibitor will stick to the metal surface more easily.

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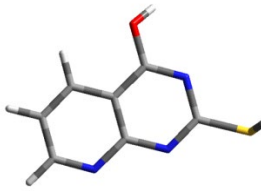
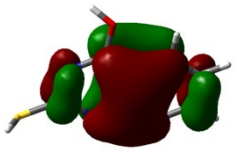
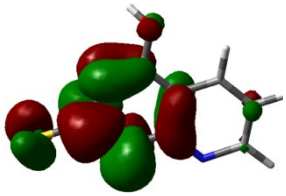
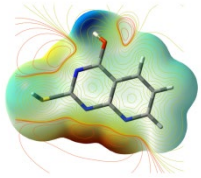
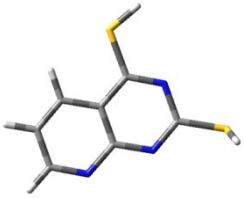
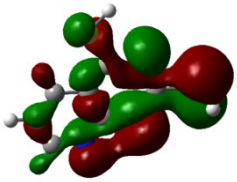
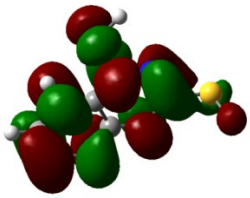
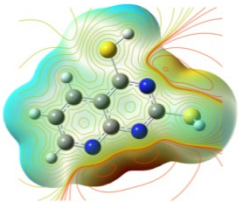
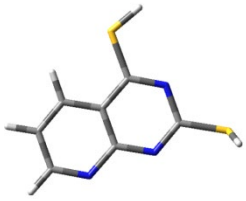
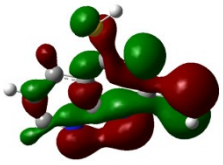
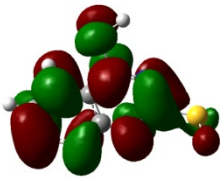
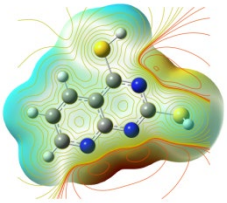
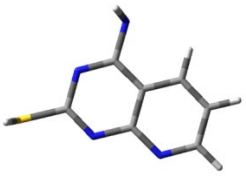
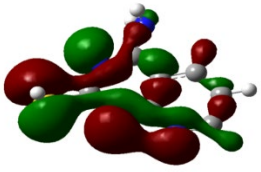
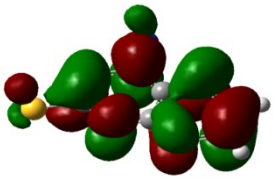
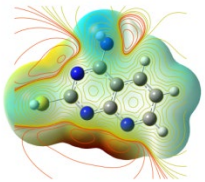
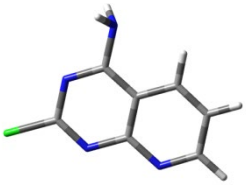
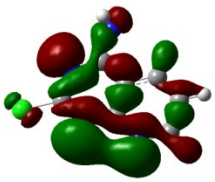
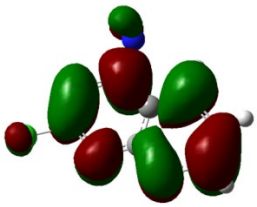
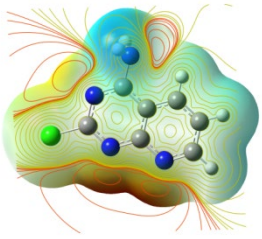
1				
2				
3				
4				
5				

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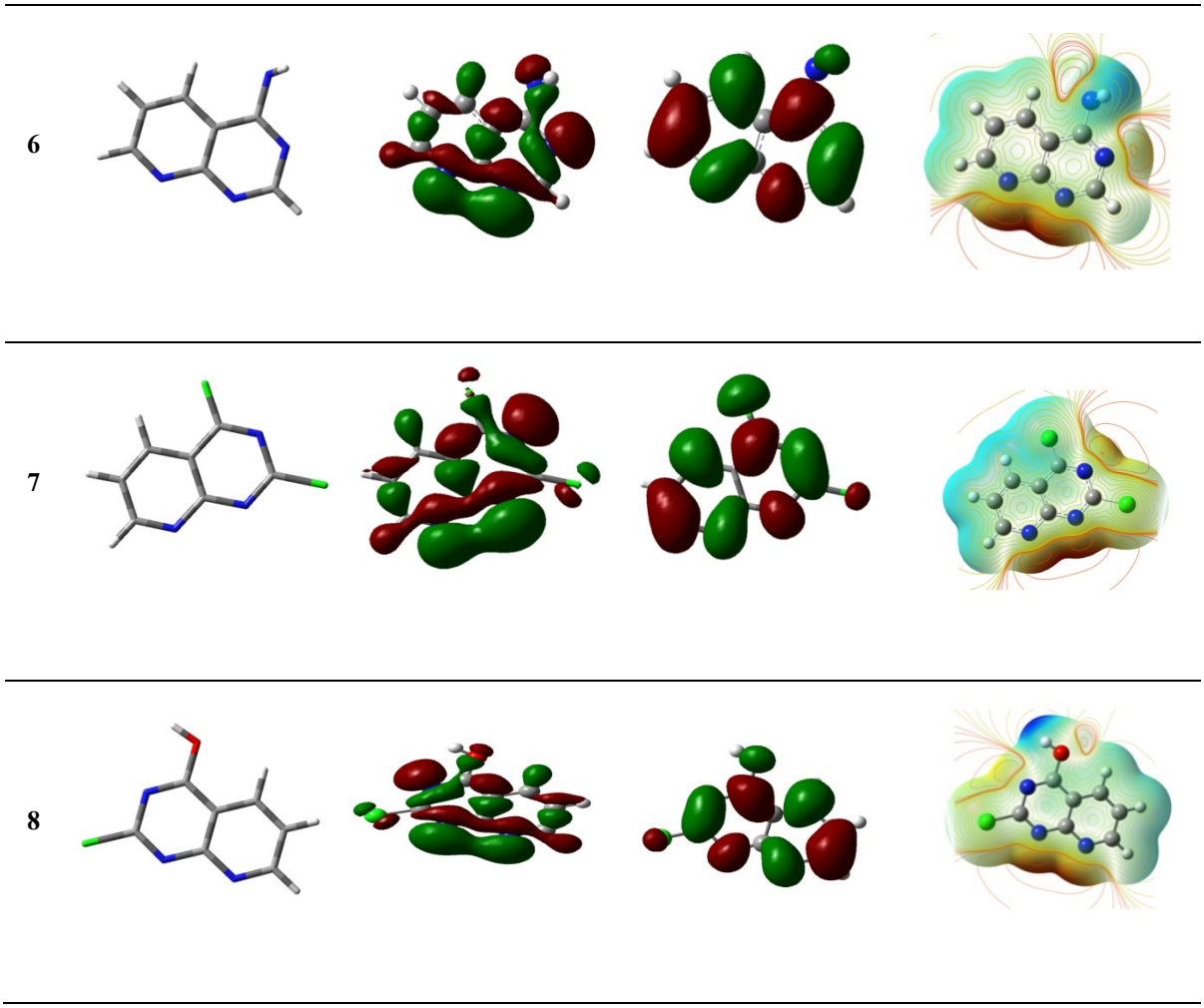

Figure 2. Structures, HOMO-LUMO diagrams and MEPs of optimized pyrimidine molecules

Table 1. Calculated quantum chemical parameters of the studied molecules in gas phase (e*V)*

Compound	E_{HOMO}	E_{LUMO}	ΔE	I	A	η
1	-7.4868	-0.9317	6.5551	7.4868	0.9317	6.5551
2	-6.6661	-2.6284	4.0377	6.6661	2.6284	4.0377
3	-6.6661	-2.6284	4.0377	6.6661	2.6284	4.0377
4	-2.5054	-6.5883	-4.0829	2.5054	6.5883	-4.0829
5	-2.5252	-6.8149	-4.2897	2.5252	6.8149	-4.2897
6	-2.2849	-6.5208	-4.2359	2.2849	6.5208	-4.2359
7	-6.9309	-2.7076	4.2233	6.9309	2.7076	4.2283
8	-6.9689	-2.4523	4.5166	6.9689	2.4523	4.5166

Compound	S	χ	μ	ω	ΔN	$\Delta E_{back\text{-}donation}$
1	0.1526	4.2093	4.4935	1.5169	0.2129	-1.6388
2	0.2477	4.6472	4.2138	2.1988	0.2914	-1,0094

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Table1 continued

3	0.2477	4.6477	4.2240	2.2095	0.2913	-1,0094
4	-0.2449	4.5469	4.8316	-2.8588	-0.2655	1,0207
5	-0.2331	5.9326	5.0226	2.9404	-0.1244	1.0725
6	-0.2360	4.4028	3.8636	-1.7621	-0.3065	1.0589
7	0.2365	4.8193	5.3886	3.4336	0.2579	-1.0571
8	0.2214	4.7106	4.6964	2.4417	0.2528	-1.1292

The inhibition properties of organic molecules also depend on the chemical hardness (η) and chemical softness (σ) of the molecule. The term chemical hardness (η) is used against electron cloud polarization and chemical degradation. The chemical hardness, global softness values of the Koopman theory[8] replaced the HOMO and LUMO energy values. If hard molecules have a high ΔEgap value, this molecule is not a good corrosion inhibitor.

The global electrophilic index (ω) surveys the ability of molecules to receive electrons. As the ω value of a molecule increases, its electrophilic character increases, and as it decreases, its nucleophilic character increases. If the transferred electron (ΔN) is < 3.6, it helps to increase the inhibitory efficiency by increasing the skill of these inhibitors to donate electrons to the metal surface. [9] The highest electron fraction is connected with the best inhibitor. In the light of this information it can be said that the compounds 4, 5 and 6 may have high inhibition potential.

4. CONCLUSIONS

In this study, quantum chemical calculations of previously synthesized pyrimidine compounds[4] were studied. The electronic properties of the molecules, corrosion prevention parameters and electrostatic potential maps (MEP) properties were theoretically calculated on the DFT-B3LYP / 6-31 G (d, p) base set. As a result, it was determined that compound 4-6 is theoretically the most active structure in terms of corrosion prevention potential.

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Conflict of interests

Authors declare that there is no a conflict of interest with any person, institute, company, etc.

REFERENCES

1. Awad, H.S.; Gawad, S.A. AntiCorros. Method Mater., 2005, 52, 328.

2. Frisch, M. J. at. al. Gaussian, Inc., Wallingford CT, 2009.

3. Shojaie, F.; Mirzai-Baghini, N. *International Journal of Industrial Chemistry*. **2015**, 6, 297–310.

4. Robins, R. K.; Hitchings, G. H. *J. Am. Chem. Soc*. **1955**, 77, 8, 2256–2260.

5. Akbas, E.; Yildiz, E.; Erdogan, A. *Journal of the Serbian Chemical Society*. **2020**, 85, 481.

6. Usman, B.; Jimoh, I.; Umar, B. A. *Applied Journal of Environmental Engineering Science*. **201**9, 5(1), 66-74.

7. Sanderson, R.T. Chemical bond and bond energy, Academic Press, New York, 1976.

8. Koopmans, *T. Physica*. 1993, 1, 104-113.

9. Ergan, E.; Akbas, E. *Fresenius Environmental Bulletin*. **2018**, 27(12B), 9549-9556.