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Potansiyel Korozyon İnhibitörü Olarak Pirimidin Türevlerinin DFT Hesaplaması ile Teorik Çalışmalar

Erdem ERGAN[1*]

ÖZET: Bu çalışmada pirimidin türevlerinin (**1-12**) korozyon önleme davranışları teorik kuantum kimyasal hesaplaması ile incelenmiştir. Tüm bileşikler için, moleküler elektrostatik potansiyel haritaları (MEP), En Yüksek İşgal Edilen Moleküler Orbital (HOMO), En Düşük Boş Moleküler Orbital (LUMO), elektronegatiflik (χ), kimyasal potansiyel (μ), global elektrofiliklik indeks (ω) ve kimyasal sertlik (η) gibi teorik hesaplamalarla elde edilen kuantum kimyasal parametreleri B3LYP / 6-31G (d, p) seviyesinde yoğunluk fonksiyonel teorisi (DFT) kullanılarak hesaplandı. Ayrıca, demir yüzeyi ile pirimidin türevi bileşikler arasında transfer edilen elektronların (ΔN) fraksiyonu hesaplandı. Bununla birlikte, doğrusal olmayan optik (NLO) özellikler de incelenmiştir. Teorik hesaplamalarla elde edilen kuantum kimyasal parametreleri incelendiğinde, bileşik **10**'un düşük ΔE_{gap} (E_{HOMO}-E_{LUMO}), kimyasal sertlik (η) değerleri ve yüksek global elektrofilik indeksi, "ΔN" değerleri ile iyi bir korozyon önleyici olarak kullanılabileceğini göstermiştir.

Anahtar Kelimeler: Pirimidin, korozyon inhibisyonu, dft, homo-lumo

Theoretical Studies *via* DFT Calculation of Pyrimidine Derivatives as Potential Corrosion Inhibitor

ABSTRACT: In this work, the corrosion prevention behaviors of pyrimidine derivatives (**1-12**) were investigated by theoretical quantum chemical calculation. Quantum chemical parameters obtained by theoretical calculations such as the Highest Occupied Molecular Orbital (HOMO), Lowest Empty Molecular Orbital (LUMO), molecular electrostatic potential maps (MEP), electronegativity (χ), chemical potential (μ), global electrophilicity index (ω), chemical hardness (η) and global softness (σ) for all compounds were studied using density functional theory (DFT) at the B3LYP / 6-31G (d, p) level. Also, the fraction of transferred electrons (ΔN) between the iron surface and the pyrimidine derivatives compounds were calculated. However, nonlinear optical (NLO) properties have also been investigated. When the quantum chemical parameters obtained by theoretical calculations are examined, it has shown that compound **10** can be used as a good corrosion inhibitor with small ΔE_{gap} (E_{HOMO}-E_{LUMO}), chemical hardness (η) values and high global electrophilicity index (ω), "ΔN" values.

Keywords: Pyrimidine, corrosion inhibition, dft, homo-lumo

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INTRODUCTION

Metal corrosion is a major problem in industries which is widely used water, alcohol, or acidic solution. A wide variety of methods are used to prevent corrosion in industry. There are five basic methods in corrosion control: material selection, coatings, inhibitors, cathodic protection, and design. Cathodic protection of metals is a frequently used method. In this method, electrons are sent to the metal surface and as a result, the cathode reaction accelerates, while the anode reaction, which proceeds in the form of dissolution of the metal, slows down. Anodic protection can only be applied to metals or alloys that show passivity in contact with the relevant electrolyte (Davis, 2000).

Corrosion inhibitors are substances that, when added to the environment in small amounts, interact with the metal surface or the environment, reducing the corrosion rate or preventing corrosion. Inhibitors generally adsorb to the metal surface, forming a protective film layer. They show activity by dissolving or dispersing in the medium. While reducing the corrosion rate, they change the anodic or cathodic polarization behavior, reduce the diffusion of ions to the metal surface, and increase the electrical resistance of the metal surface. (Roberge, 2000).

Heterocyclic structures containing nitrogen, sulfur, oxygen, and aromatic rings are widely used as corrosion inhibitors for metals in acidic environments. When the corrosion studies with pyrimidine compounds were examined, the researchers found that these compounds absorb metal surfaces, block active zones and thus reduce the effect of corrosion. Corrosion inhibition activities of pyrimidine compounds rely on the number of unpaired electron pairs (Arora et. al., 2007), the π orbital character of free electrons (Hackerman and Hurd, 1960), and the electron density on nitrogen atoms (Riggs and Every, 1962). In addition, the presence of scaffolds connected to the pyrimidine ring affects corrosion inhibition potentials. Heakal et al. (2018) examined the theoretical inhibition efficiency of imidazole-pyrimidine compounds. They explained the inhibition efficiency with the decrease of ΔE_{gap} (HOMO - LUMO energy difference) and the increase of molecular surface area.

With the improvement of computer hardware and software, density functional theory (DFT) and molecular dynamics simulation methods have recently become fast and powerful tools to predict the corrosion inhibition efficiency of inhibitor molecules. The use of theoretical parameters helps to characterize the molecular structure of inhibitors and to suggest their interactive mechanisms with surfaces. Quantum chemical studies give preliminary information about the activities of molecules. Parameters concerned to the reactivity of molecules with density functional theory (DFT) in quantum chemical calculations; HOMO, LUMO, electronegativity (χ), chemical potential (μ), global electrophilicity index (ω) and chemical hardness (η) are calculated (Dutta et al., 2017).

In this study, the theoretical corrosion inhibition potentials of previously synthesized pyrimidine compounds (Figure 1) (Dam et. Al., 2017) were investigated using density functional theory (DFT) at the B3LYP / 6-31G (d, p) level. With this calculation, quantum chemical parameters, geometric optimizations, and electrostatic potential maps (MEP) of the compounds were obtained.

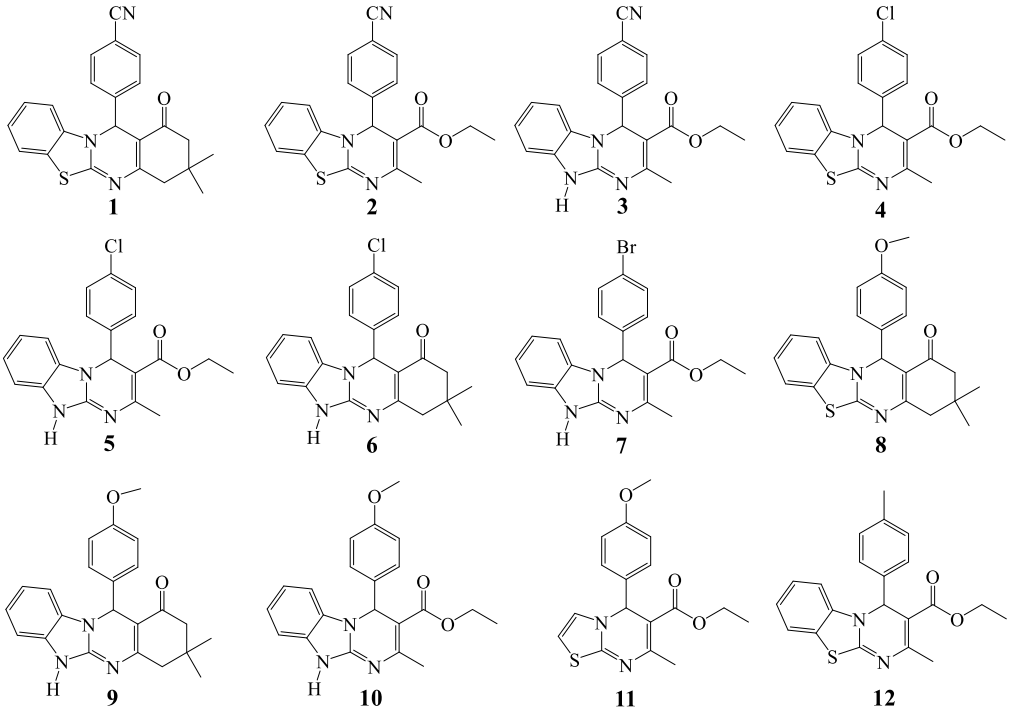


Figure 1. Molecular structures and schematic representation of pyrimidine derivatives

MATERIALS AND METHODS

Method of Calculation

DFT method is one of the most preferred methods used in calculating the reactivity of molecules. In this study, quantum chemical calculations of previously synthesized pyrimidine derivatives (Figure 1) (Dam, 2017) were performed using Gaussian 09W software. In this program, density functional theory (DFT) and Becke's three-parameter change function, and Lee-Yang-Parr non-local correlation function (B3LYP) 6.31 G (d, p) base set is used (Lee, 1988; Becke, 1993; Frisch, 2010).

Computational Details

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 calculations have demonstrated that the molecule's HOMO and LUMO 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 E_{HOMO}, E_{LUMO}, ΔE_{gap} (HOMO-LUMO energy gap), electronegativity (χ), chemical potential (μ), chemical hardness (η), global electrophilicity index (ω), global softness (σ) (Ergan and Akbas, 2018).

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

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

The ionization energy (I) and electron affinity (A), electronegativity (χ), global softness (σ) and chemical hardness (η) values of the studied molecules are obtained by HOMO and LUMO energy, and the following equations are obtained (Brus, 1983):

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

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

Global softness (σ) is a chemical illustrator that surveys molecular stability and reactivity. Global softness (σ) is described as the reverse of chemical hardness (η), (Chattaraj et. al., 2006).

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

The global electrophilicity index (ω) is a survey of the energy drop because of the maximum electron run between donor and acceptor. It may be represented as a function of electronegativity (χ) and chemical hardness (η) as shown in Eq. (6), (Parr and Yang, 1989).

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

The global electrophilicity index (ω) surveys the skill 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 (Sanderson, 1954; Sanderson, 1976), the value of the electrons transferred from the anti-corrosion molecule is calculated by the following equation.

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

The χ_M and χ_{inh} values shown in Equation 7 correspond to the electronegativity values of the metal and the inhibitor molecule, respectively, while the η_M and η_{inh} values represent the chemical hardness values of the metal and the inhibitor molecule.

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 (Ramírez-Ramírez et. al., 2010).

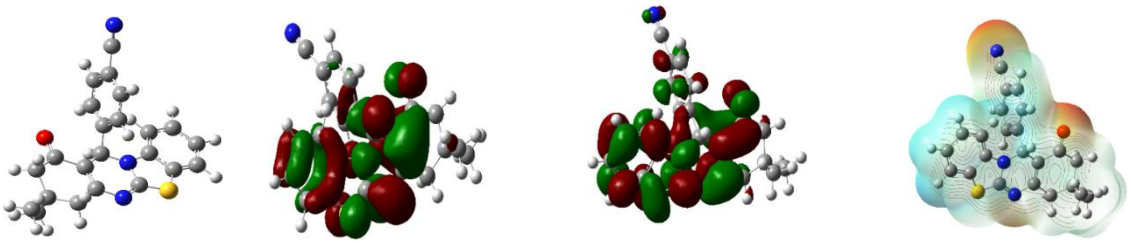
$$\Delta E_{back\ donation} = -\frac{\eta}{4} \quad (8)$$

RESULTS AND DISCUSSION

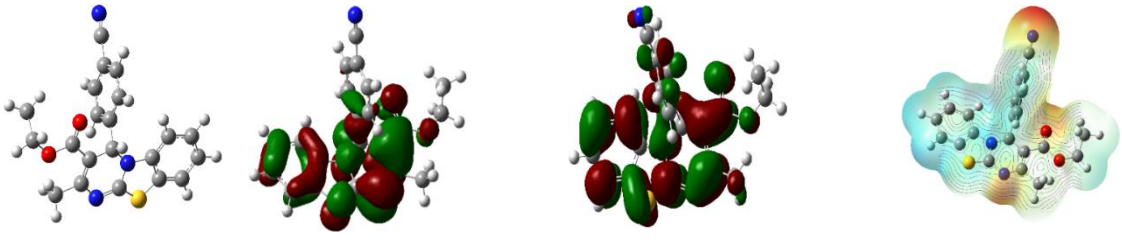
Fully geometric optimizations of all molecules, HOMO-LUMO diagrams, MEP, and corrosion inhibition parameters were arranged with density functional theory (DFT) and B3LYP (d, p) base set in Gaussian09 program. (Figure 2 and Table 1). It has been determined in some studies that this calculation method, which is carried out theoretically, is used to examine the concern between corrosion inhibition effectiveness and electronic properties of molecules (Young, 2001).

Geometric optimizations of all molecules, HOMO and LUMO diagrams, and MEP are shown in Figure 2. MEPs have been used to interpret and predict the relative reactivity of electrophilic and nucleophilic attack domains, investigate biological recognition, interactions of hydrogen bonds, zeolite studies, molecular cluster and crystal behavior, and correlation and prediction of a wide variety of macroscopic properties (Ravikumar et. al., 2008).

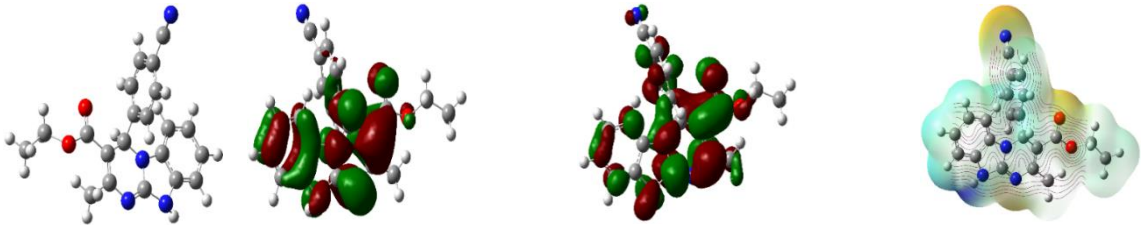
Electrostatic potential maps (MEP) that provide information about the molecular distribution of electrons are represented by different colors. In Figure 2, the negative (red) areas of the MEP are associated with electrophilic reactivity and positive (blue) areas with nucleophilic reactivity. Electrostatic potential increases during red> orange> yellow> green> blue. The highest potential is on oxygen atoms (Zhang, 2018).



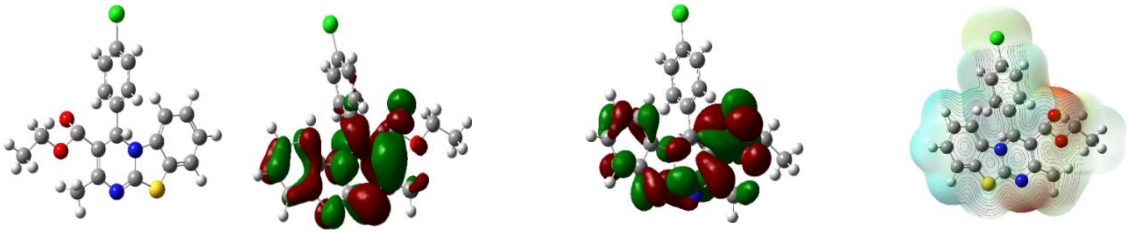
1 **HOMO** **LUMO** **MEPs**



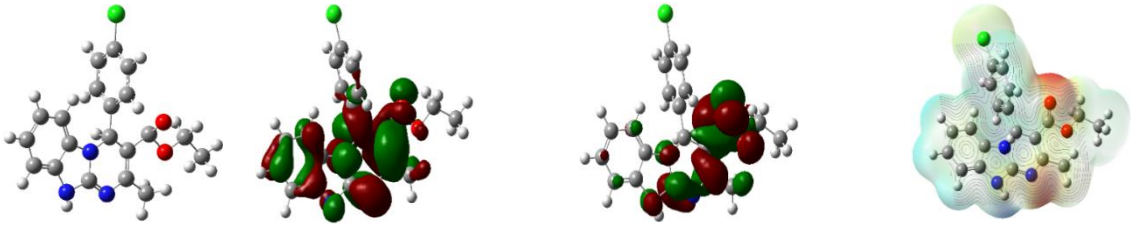
2 **HOMO** **LUMO** **MEPs**



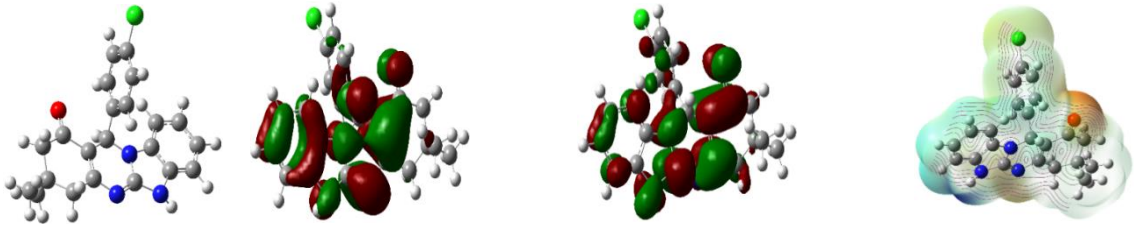
3 **HOMO** **LUMO** **MEPs**



4 **HOMO** **LUMO** **MEPs**



5 **HOMO** **LUMO** **MEPs**



6 **HOMO** **LUMO** **MEPs**

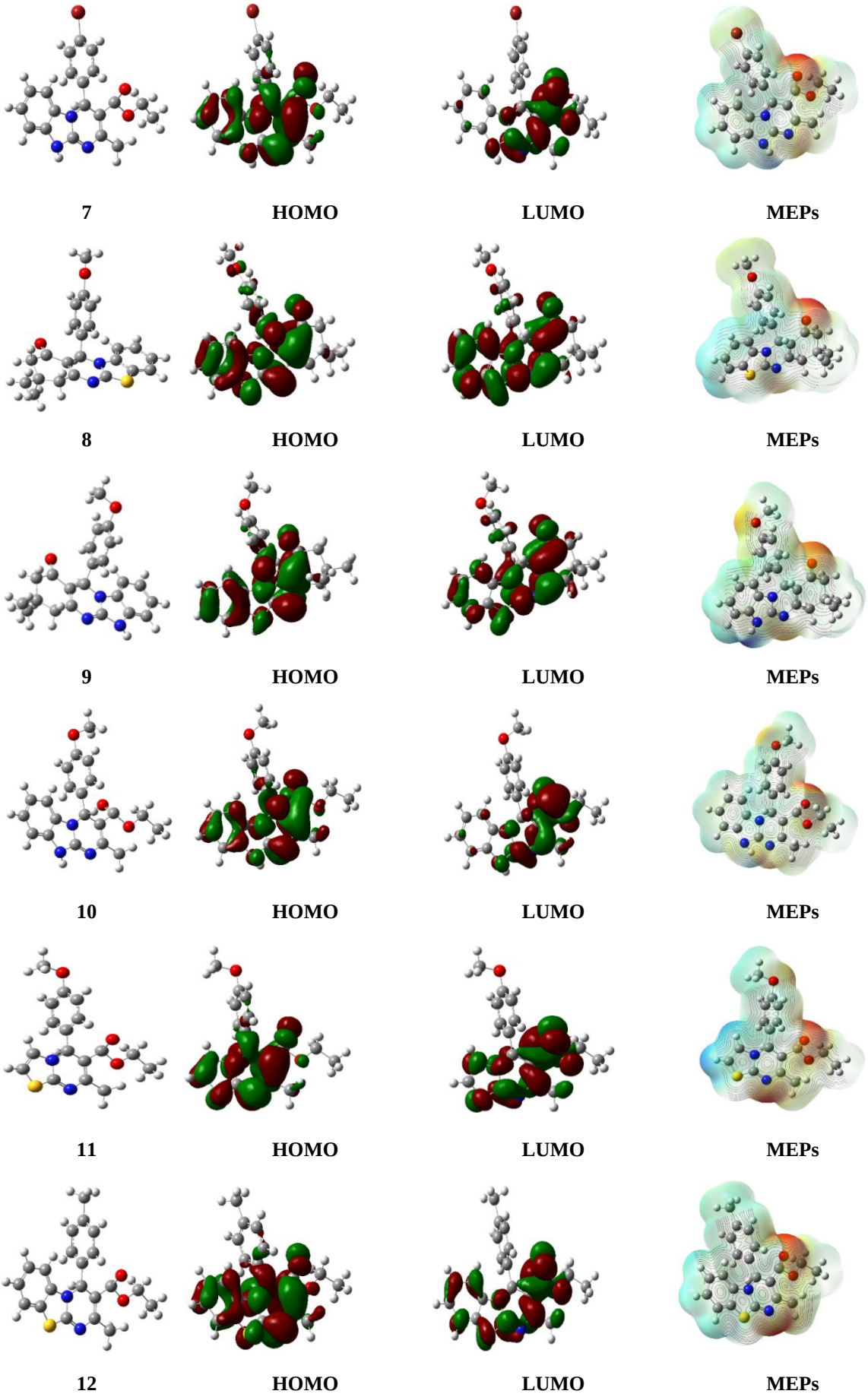


Figure 2. Structures, HOMO-LUMO diagrams, and MEPs of optimized pyrimidine molecules

Table 1. Calculated quantum chemical parameters of the studied molecules with the B3LYP method in the gas phase (eV)

	E_{HOMO}	E_{LUMO}	ΔE_{gap}	I	A	η	σ	χ	μ	Dipole Moment	ω	ΔN	$\Delta E_{back\text{-}donation}$
1	-5.2758	-1.9644	3.3114	5.2758	1.9644	1.6557	0.6040	3.6201	-3.6201	6.7684	3.9576	1.0207	-0.4139
2	-5.2703	-1.9013	3.3690	5.2703	1.9013	1.6845	0.5936	3.5858	-3.5858	5.6317	3.8166	1.0134	-0.4211
3	-5.4815	-1.9407	3.5408	5.4815	1.9407	1.7704	0.5648	3.7111	-3.7111	7.1249	3.8896	0.9289	-0.4426
4	-4.2722	-1.9693	2.3029	4.2722	1.9693	1.1515	0.8685	3.1208	-3.1208	3.5252	4.2291	1.6845	-0.2879
5	-4.3762	-2.0433	2.3329	4.3762	2.0433	1.1665	0.8573	3.2098	-3.2098	3.0120	4.4162	1.6247	-0.2916
6	-5.2548	-1.7690	3.4858	5.2548	1.7690	1.7429	0.5738	3.5119	-3.5119	4.6559	3.5382	1.0007	-0.4357
7	-4.5174	-2.4186	2.0988	4.5174	2.4186	1.0494	0.9529	3.4680	-3.4680	3.9074	5.7304	1.6829	-0.2624
8	-5.1133	-1.8039	3.3094	5.1133	1.8039	1.6547	0.6043	3.4586	-3.4586	4.8407	3.6145	1.0701	-0.4137
9	-5.1351	-1.6558	3.4793	5.1351	1.6558	1.7397	0.5748	3.3955	-3.3955	2.6958	3.3136	1.0360	-0.4349
10	-4.4575	-2.3775	2.0800	4.4575	2.3775	1.0400	0.9615	3.4175	-3.4175	2.2321	5.6151	1.7224	-0.2600
11	-3.9666	-1.6493	2.3173	3.9666	1.6493	1.1587	0.8631	2.8080	-2.8080	5.9711	3.4025	1.8090	-0.2897
12	-4.1032	-1.8161	2.2871	4.1032	1.8161	1.1436	0.8745	2.9597	-2.9597	4.6252	3.8300	1.7666	-0.2859

Corrosion inhibitory activities of pyrimidine derivatives were studied by quantum chemical calculation. The chemical reactivity of the studied molecules was obtained from the Gaussian software program. Corrosion inhibition parameters of the studied molecules like $E_{HOMO,}$ E_{LUMO}, ΔE_{gap} (HOMO-LUMO energy gap), ionization energy (I), electron affinity (A), electronegativity (η), chemical potential (μ), chemical hardness (η), global softness (σ), global electrophilicity index (ω) and the fraction of transferred electrons (ΔN) were investigated (Table 1).

These parameters are very significant parameters used in comparing the chemical reactivity of the molecules examined. 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 E_{HOMO} value shows a better tendency to electron donation and increases the adsorption on the metal. Therefore, it provides a better inhibition efficiency. The LUMO energy level of molecules is the molecule's ability to accept electrons. When the LUMO energy level of the inhibitor molecule is lower, it is capable of accepting more electrons. The skill of the inhibitor to bind to the metal surface increases with increasing HOMO energy value and decreasing LUMO energy value (Zarrouk et. al., 2014).

The energy gap (ΔE_{gap}) between the E_{HOMO} and E_{LUMO} energy levels of molecules is one of the most important parameters used to determine the reactivity of the inhibitor molecule. The fact that the inhibitor molecule has a small ΔE_{gap} is an indication that that molecule is a good corrosion inhibitor. Also, the ΔE_{gap} of the inhibitor molecule indicates its ability to bind to the metal surface (Pearson, 1963). When the ΔE_{gap} values of the pyrimidine molecules in Table 1 are compared, their corrosion prevention activities can be listed as follows: **10> 7> 12> 4> 11> 5> 8> 1> 2> 9> 6> 3**.

The term chemical hardness (η) (Pearson, 1968; Sanderson, 1976; Koopmans, 1993; Makov, 1995) is used against electron cloud polarization and chemical degradation. Chemical hardness (η) is a significant parameter investigating the reactivity of molecules in experimental and theoretical chemistry. If hard molecules have a high ΔE_{gap} value, this molecule is not a good corrosion inhibitor. Therefore, this molecule cannot easily donate HOMO's electron to metal. Global softness (σ), $\Delta E_{gap,}$ and chemical hardness are interrelated. The chemical hardness, global softness values of the Koopmans theory (Koopmans, 1993) replaced the HOMO and LUMO energy values. When the chemical hardness values in Table 1 are examined, their potential to be a corrosion inhibitor can be listed as follows: **10> 7> 12> 4> 11> 5> 8> 1> 2> 9> 6> 3**.

The global electrophilicity index (ω) surveys the skill 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. It can be said that **7** and **10** compounds with high electrophilicity values have high inhibition potential.

If the transferred electron (ΔN) is < 3.6, it helps to increase the inhibitory efficiency by increasing the skill of these inhibitors to give electrons to the metal surface (Lukovits et. al., 2001). There is a direct proportion between electron fraction and inhibition. Increasing electron fraction indicates it will be a good inhibitor. I would say that compounds **10, 11,** and **12** have high electron fractions and their inhibition efficiency is high.

$\Delta E_{back\ donation}$ calculated according to Eq. (8). This value is related to chemical hardness. When the values of $\Delta E_{back\ donation}$ are examined, it shows that back donation is preferred as the best inhibitor of **10**.

When the calculated parameters are examined in general, it can be said that compound **10** has better anti-corrosion potential than other compounds.

The nonlinear optical properties of pyrimidine compounds **1-12** were performed in the gas phase using the B3LYP / 6-31G (d, p) base set. (Table 2a and 2b). Dipole moment is an important property of the energy associated with the applied electric field in the molecule. Intermolecular interactions involving van der Waals type dipole-dipole forces cause dipole moment. Using the equations given below (9-11), the total dipole moment μ_{tot}, the average polarizability (α_{tot}), and the mean value of the initial hyperpolarizability can be found.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (9)$$

$$\alpha_{tot} = 1/3\ (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (10)$$

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yxx} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \quad (11)$$

Table 2a. Electric dipole moment μ (D), polarizability α_{tot} (10^{-24} esu) and first hyperpolarizability β_{tot} (10^{-32} esu) values for molecules 1-6 obtained by B3LYP level with the 6-31 G (d,p) basis set.

Parameters	1	2	3	4	5	6
β_{xxx}	-3.080	-34.598	-27.807	-1.070	-30.165	4.662
β_{xyy}	64.577	-50.341	-10.525	18.895	21.534	-37.093
β_{xzz}	-8.068	4.243	-15.298	-18.499	-17.075	-13.327
β_{yyy}	-276.292	-235.749	-296.857	3.153	-30.988	-96.516
β_{yxx}	-90.386	-54.374	-76.044	-30.519	-12.472	-38.072
β_{yzz}	1.548	-0.048	12.933	17.313	22.693	21.346
β_{zzz}	0.167	-4.270	-9.191	-1.801	-1.132	1.361
β_{zxx}	25.259	-6.807	-35.934	8.479	-17.075	17.670
β_{zyy}	51.895	-92.353	-71.755	-3.611	15.255	-8.842
β_{tot} (esu) 10^{-32}	325.753	275.136	330.260	9.100	28.666	105.892
α_{xx}	-151.871	-134.762	-125.565	-141.429	-139.921	-148.810
α_{yy}	-202.898	-199.098	-189.741	-179.743	-166.463	-164.341
α_{zz}	-166.494	-159.224	-152.831	-158.932	-153.335	-163.763
α_{tot} (esu) 10^{-24}	-25.746	-24.354	-23.122	-23.713	-22.706	-23.556
μ_x	-1.498	-4.366	2.458	3.139	1.955	-1.291
μ_y	-6.542	-2.969	-6.015	0.583	-0.439	-4.464
μ_z	0.878	-1.959	-2.923	1.494	2.249	0.296
μ_{tot} (D)	6.768	5.632	7.125	3.525	3.012	4.656

Table 2b. Electric dipole moment μ (D), polarizability α_{tot} (10^{-24} esu) and first hyperpolarizability β_{tot} (10^{-32} esu) values for molecules 7-12 obtained by B3LYP level with the 6-31 G (d,p) basis set.

Parameters	7	8	9	10	11	12
β_{xxx}	152.142	6.984	-2.918	-18.687	-112.560	-3.576
β_{xyy}	2.078	-4.242	-46.520	-29.991	23.884	16.054
β_{xzz}	56.595	-16.692	-6.424	-19.246	-13.433	-18.215
β_{yyy}	-9.357	-105.386	28.247	49.443	54.976	89.781
β_{yxx}	-16.460	-57.219	-52.165	-20.428	1.280	-28.718
β_{yzz}	-32.540	11.789	18.486	17.233	-9.059	7.916
β_{zzz}	0.073	-2.092	0.379	2.471	-2.136	-2.268
β_{zxx}	-9.352	25.068	17.445	-5.846	-2.699	8.580
β_{zyy}	-19.662	3.853	-0.260	10.353	5.410	-1.745
β_{tot} (esu) 10^{-32}	190.640	132.897	50.811	71.253	97.192	59.933
α_{xx}	-169.641	-157.275	-149.432	-134.963	-143.327	-137.989
α_{yy}	-143.333	-180.596	-150.946	-156.722	-123.082	-156.151
α_{zz}	-160.016	-168.194	-165.186	-154.686	-136.353	-155.152
α_{tot} (esu) 10^{-24}	-23.362	-24.996	-22.995	-22.047	-19.893	-22.191
μ_x	-0.076	-1.764	-1.293	1.665	-3.818	3.040
μ_y	2.855	-4.504	-2.285	0.78	4.326	3.139
μ_z	-2.666	0.193	0.613	-1.265	1.535	1.517
μ_{tot} (D)	3.907	4.841	2.696	2.232	5.971	4.625

CONCLUSION

In this study, quantum chemical calculations of previously synthesized pyrimidine compounds (Dam, 2017) were studied. The electronic properties of the molecules, corrosion prevention parameters, electrostatic potential maps (MEP), and NLO properties were theoretically calculated on the DFT-B3LYP / 6-31 G (d, p) base set. In the light of the information given in the tables and figures, the corrosion prevention potentials of the pyrimidine molecules were theoretically examined and it was determined that compound **10** could be the most active. In addition, compounds **1** and **3** were found to be the most active compounds in terms of NLO properties.

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Conflict of Interest

I declare that there is no conflict of interest during the planning, execution, and writing of the article.

Author's Contributions

I hereby declare that the planning, execution, and writing of the article were done by me as the sole author of the article.

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