Dear Editor,

We appreciate the opportunity to revise and resubmit our paper titled “**Synthesis, characterization and electrochemical properties of novel pyrimidine derivatives as potential corrosion inhibitors agents**“. We want to thank the editor and reviewer(s) for helpful comments and revision recommendations. We have revised our present research paper in the light of their useful suggestions and comments. We hope that the revision is acceptable.

Yours sincerely,

Prof. Dr. Esvet Akbas

We have modified the manuscript accordingly, and the detailed corrections are listed below point by point: and **all changes are marked with colors.** In additon we sending manuscrip\_clean file as attachet file.

**Reviewer 1**

English should be significantly improved through the all manuscript.

**Response**: In the main text was done

The word “some” is not necessary in the manuscript title.

**Response**: In the main text was done

Abstract: instead “compound 6” full name of the compound should be  
written.

**Response**: In the main text was done

Introduction: - Line 52: the sentence “The quantum chemical calculations (QCCs) have  
been widely used in the reactivity of organic compounds” for corrosioninhibition should be supported by relevant references, 

**Response**: In the main text was done

Line 56: the part of sentence “The high  EHOMO value has a compound tendency to give electrons” is not correct

**Response**: In the main text was done

Line 58: the a part of sentence “low reactivity to a chemical interaction” is not meaningful and should be corrected

**Response**: In the main text was done

Experimental:  
-The meaning of subtitle “Chemistry”  is not appropriate.

**Response**: In the main text was done

The experimental part regarding syntheses of compounds is not clearly written (e.g. sentence construction “To a solution of (4,6-diphenyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-102 yl)(phenyl)methanone 8 (2) (1 mmol) and ethyl 2-bromoacetate (1 mmol) was refluxed for 6 h 103 in dioxan (10 mL) /presence of catalytic amount of pyridine (1mL) is not grammaticaly correct and clear).

**Response**: In the main text was done

Conclusion is too concise and should be rewritten.

**Response**: In the main text was done

Results and discussion:11. Line 215: It is written Tab. 2, however the manuscript contains only Table1.

**Response**: In the main text was done

Line 233:  term Highest Occupied Molecular Orbital is first time mentioned in line 233, but the abbreviation HOMO is used many times before. Similar remark is for LUMO. The abbreviations should be introduced at first place of appearance in the text.

**Response**: In the main text was done

Line 240: the sentence “Similar relations were found between the rates of corrosion and ΔE (ΔE = ELUMO−  EHOMO)” is not clear.

**Response**: In the main text was done

Line 272. It is not enough for the reader to shortly concluded that “According to the calculations, the compound 6 appears to be a good inhibitor for corrosion” but decisive factors should be farefareffdfsd in detail for this compound.

**Response**: In the main text was done

The connection of the text given in the section Molecular electrostaticpotentials (MEP) with corrosion inhibition is not clearly presented.

**Response**: In the main text was done

**REVIEWER 2**

Line 8: In this study, seven new chiral pyrimidine derivatives were this must be five pirimidin derivatives

**Response**: In the main text was done

Line 114: A mixture of 59 (1 mmol), benzaldehyde Ref. 9 must be corrected

**Response**: In the main text was done

Line 142: acid9 (9) Ref. 9 must be corrected

**Response**: In the main text was done

Line 130: N-phenylure this must be N-phenylurea

**Response**: In the main text was done

Yours sincerely,

Prof. Dr. Esvet Akbas

**Synthesis, characterization and electrochemical properties of novel pyrimidine derivatives as potential corrosion inhibitors agents**

**ESVET AKBAS1,\*, ELA YILDIZ1 AND AHMET ERDOGAN1**

**1***Department of Chemistry, Van Yuzuncu Yil University, 65080, Van, Turkey.*

*Abstract:*In this study, five new pyrimidine derivatives were synthesized and characterized by characterization methods such as 1H-NMR, 13C-NMR, FT-IR and elemental analysis. The corrosion inhibition activity of synthesized compounds was examined with theoretical calculation using DFT method at the level of B3LYP / 6-31G (d, p). According to the calculations, 4-(6-benzoyl-2-benzylidene-3-oxo-7-phenyl-3,5-dihydro-2H-thiazolo[3,2-a]pyrimidin-5-yl)benzoic acid (**6**) appears to be a good inhibitor for corrosion.

*Keywords:* corrosion inhibition; DFT; pyrimidine; characterization

**INTRODUCTION**

Pyrimidines and their derivatives are of special importance organic compounds because of their versatile medicine, agrochemicals and in many biological processes. Several pyrimidine derivatives exhibit a diverse array of biological and pharmacological activities including anticonvulsant, antibacterial, antifungal, antiviral and anticancer properties.1 This broad spectrum of biochemical targets has been enabled by the synthetic versatility of pyrimidine, which has allowed derivatisation of the ring nitrogens and C2/C4/C5/C6 carbon positions.2 Pyrimidine derivatives constituted many well established marketed drugs such as Uramustine, Piritrexim, Isetionate, Tegafur, Floxuridine, Fluorouracil, Cytarabine and Methotrexate etc. Moreover, Pyrimidine skeleton (mainly uracil, thiamine and cytosine) are essential part in many natural products such as nucleic bases, vitamins, enzymes, chlorophyll, hemoglobin and hormones. 2

The wide variety of biological activities observed for these compounds turned pyrimidine derivatives as environmentally benign compounds. The requirement for good corrosion inhibitor, i.e., organic compounds which can donate electrons to unoccupied d-orbital of metal surface to form coordinate covalent bonds and can also accept free electrons from the metal surface by using their anti-bonding orbital to form feedback bonds, is also

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

\*Corresponding author E-mail: esvakbas@hotmail.com

fulfilled by pyrimidine molecule. Hence pyrimidine derivatives are expected to be excellent corrosion inhibitors at industrial level, not only due to their efficiency but also due to their non-toxic nature. 1

Acidic environments are widely used in several industrial operations, such as oil well acidification, acid pickling, acid cleaning and acid descaling, which generally lead to serious metallic corrosion. Despite the relatively limited corrosion resistance of carbon steel, it is widely used in marine applications, chemical processing, petroleum production and refining, construction and metal-processing equipment due to its excellent mechanical properties and low cost. Out of several methods, usage of corrosion inhibitor is one of the most important techniques for controlling the corrosion. Many organic inhibitors have been tried for the corrosion inhibition of steel, out of which organic compounds with more than one heteroatom containing π-electrons are found to exhibit high inhibiting properties by providing electrons which interact with metal surface. 3 However, the use of several heterocyclic inhibitors has caused negative effects on the environment because of their toxicity and nonbiodegradability. In this context, pyrimidine derivatives are found to attract great interest due to their environmentally benign properties.4a

The quantum chemical calculations (QCCs) have been widely used in the reactivity of organic compounds for corrosion inhibition.4b In this work, the theoretical calculations for the inhibition potentials were explained using QCCs based on Density Functional Theory (DFT). The EHOMO and ELUMO energies of the molecules were calculated in the Gaussian09.5

The effectiveness of an inhibitor can be related to not only its spatial molecular structure, but also with their molecular electronic structure. According to frontier orbital theory, the reaction of reactants mainly occurred on Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO), and the formation of a transition state is due to an interaction between the frontier orbitals of the reactants. So, it was important to investigate the distribution of HOMO and LUMO for exploration of inhibition mechanism. Organic substances with a higher energy level of HOMO easily donate electrons from HOMO to an empty orbital of appropriate acceptors and ELUMO denotes the ability of the molecule to accept electrons.

The difference between ELUMO and EHOMO energies is called energy gap (ΔE). It was generally acknowledged that low values of ΔE will provide good inhibition efficiency, because the energy for removing an electron from the last occupied orbital will be low.6a

.For the theoretical calculation of the inhibitory effect of a molecule, it is necessary to know the ionization potential (I), the electron affinity (A), the chemical hardness-softness (S), the global electrophilicity index (ω), the interaction between the transmitted electron fraction index (ΔN) and the interaction between back donations. All these values calculated according to Shojaie et al. 6b

**EXPERIMENTAL**

*Chemicals and Instruments*

All chemicals and solvents used in the experiments were assured from Turkey representative of Sigma Aldrich (St. Louis, MO) and Fluka (Buchs, Switzerland). All reactions were monitored by thin layer chromatography (TLC). TLC plates were based on silica gel 60 F254 aluminum plates with a 0.2 mm layer thickness (Merck Co., Darmstadt, Germany). The spots in TLC were determined by UV lamp. Stuart (UK) SMP30 melting point apparatus was used to measure the melting points of the synthesized compounds. FT-IR spectra of compounds were measured in the range of 4000-400 cm-1 by using a Perkin Elmer Spectrum 100 FT-IR

Spectrometer (universal ATR sampling accessory). 1H and 13C nuclear magnetic resonance (NMR) spectra of compounds were measured in DMSO*d*6 by using a Bruker (Billerica, MA) AVANCDPX-400 MHz spectrometer at 400 MHz and 100 MHz, respectively. Tetramethylsilane (TMS) was used as the internal reference. Elemental analyses were determined by using a Thermo Scientific (Pittsburgh, PA) Flash 2000 elemental analyzer. Full geometry optimizations of the all molecules were performed using Gaussian09.

*Synthesis*

*Ethyl 2-(5-benzoyl-4-(3-nitrophenyl)-6-phenyl-3,4-dihydropyrimidin-2(1H)-ylidene)acetate (****3****).*

To a solution of (4-(3-nitrophenyl)-6-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl)(phenyl)methanone7 (**1**) (1 mmol) and ethyl 2-bromoacetate (1 mmol) was refluxed for 6 h in dioxan (10 mL) /presence of catalytic amount of pyridine (1mL). Then the solvent was removed by rotary evaporator. The resulting oily substance was treated with 1:1 ratio of HCl: H2O (10 mL) and recrystallized from methanol. Yield 54%, mp 210-211ºC, FTIR (KBr/cm‒1) 3174, 3061 cm-1 (NH). 1622 and 1596 cm-1 (C=O). 1H-NMR (400 MHz, DMSOd6) δ 10.98 (s, 1H, NH), 10.12 (s, 1H, NH), 8.32-7.02 (m, 14H, Harom.), 5.47 (s, 1H, C4H), 5.32 (s, 1H, =CH), 4.45(q, 2H, OCH2), 1.16 (t, 3H, CH3). Anal. Calcd. for C27H23N3O5: C, 69.07; H, 4.94; N, 8.95. Found: C, 69.05; H, 4.96; N, 8.96.

*Ethyl 2-(5-benzoyl-4,6-diphenyl-3,4-dihydropyrimidin-2(1H)-ylidene)acetate (****4****).*

The (4,6-diphenyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl)(phenyl)methanone 8 (**2**) (1 mmol), ethyl 2-bromoacetate (1 mmol) and pyridine (1mL) was refluxed in dioxan (10 mL) with for 6 h. Then the solvent was removed by rotary evaporator. The resulting oily substance was treated with 1:1 ratio of HCl: H2O (10 mL) and recrystallized from ethanol. Yield 62%, mp 203-205ºC, FTIR (KBr/cm‒1) 3208, 3062 cm-1 (NH). 1622 and 1594 cm-1 (C=O). 1H-NMR (400 MHz, DMSOd6) δ 10.96 (s, 1H, NH), 10.11 (s, 1H, NH), 8.30-6.96 (m, 15H, Harom.), 5.44 (s, 1H, C4H), 5.30 (s, 1H, =CH), 4.33 (q, 2H, OCH2), 1.15 (t, 3H, CH3). Anal. Calcd. for C27H24N2O3: C, 76.39; H, 5.70; N, 6.60. Found: C, 76.40; H, 5.71; N, 6.58.

*4-(6-benzoyl-2-benzylidene-3-oxo-7-phenyl-3,5-dihydro-2H-thiazolo[3,2-a]pyrimidin-5-yl)benzoic acid (****6****).*

A mixture of **5**9 (1 mmol), benzaldehyde (1 mmol) and anhydrous sodium acetate (1 mmol) in glacial acetic acid (10 ml) was heated under reflux for 4 h. The reaction mixture was kept overnight and the solid, thus separated, was filtered, washed with water and recrystallized from ethanol. Yield 58%, mp. 247-248ᵒC, IR (KBr/cm-1): 1713, 1685, 1608 (C=O); 1H NMR (400 MHz, DMSOd6) δ 12.72 (bs, 1H, OH), 7.91-7.10 (m, 19H, Harom.), 6.41 (s, 1H, C4H), 4.22 (s, 1H, CH), 13C-NMR (100 MHz, DMSOd6) δ 196.1 (C=O, benzoyl), 172.5 and 167.1 (C=O), 164.7, 155.2, 147.1, 144.1, 137.6, 137.4, 133.4, 133.1, 132.9, 131.1, 131.1, 130.5, 129.8, 129.7, 129.5, 129.0, 128.3,128.2, 128.1, 120.2, 116.9, 57.6 ppm. Anal. Calcd. for C33H22N2O4S: C, 73.05; H, 4.09; N, 5.16. Found: C, 73.03; H, 4.10; N, 5.18.

*1-(4-(6-benzoyl-3-oxo-7-phenyl-3,5-dihydro-2H-thiazolo[3,2-a]pyrimidin-5-yl)benzoyl)-3-phenylurea (****8****).*

The 4-(6-benzoyl-3-oxo-7-phenyl-3,5-dihydro-2H-thiazolo[3,2-a] pyrimidin-5-yl) benzoyl chloride (**7**)was obtained by the reaction of **5** with thionylchloride. The compound **5** (1 mmol) and thionylchloride (1 mL, 13.8 mmol) were refluxed on a steam bath for 6 h. The solvent was evaporated, and then the residue was dissolved in 10 mL of xylene. Thereafter, a moderate stream of N-phenylurea and solution of compound 7 were boiled for 4 h. Then, the crude precipitate was filtered off and recrystallized from dioxane to give of compound **8**. Yield: 34%, mp 205–206ᵒC. IR (KBr) 1704, 1620, 1597 cm-1 (C=O). 1H-NMR (400 MHz, DMSOd6) δ 10.92 (bs, 1H. NH), 10.21(bs, 1H. NH), 8.0-7.1 (m, 19H, Harom.), 6.4 (s, 1H, C4H), 3.5 ppm (s, 2H, CH). 13C-NMR (100 MHz, DMSOd6) δ 195.8 (C=O, benzoyl), 167.1, 164.2(C=O), 157.2(C=O), 146.3, 135.4, 134.3, 133.2, 132.9, 131.1, 130.9, 130.4, 129.5, 129.0, 128.8, 128.4, 128.0, 127.1, 126.9, 125.4, 124.1, 120.6, 66.8, 30.8 ppm. Anal. Calcd. for C33H24N4O4S: C, 69.22; H, 4.22; N, 9.78. Found: C, 69.20; H, 4.21; N, 9.75.

*4-(7-benzoyl-4-oxo-8-phenyl-2,3,4,6-tetrahydropyrimido[2,1-b][1,3]thiazin-6-yl)-N,N-diethylbenzamide (****11****).*

The 4-(7-benzoyl-4-oxo-8-phenyl-2,3,4,6-tetrahydropyrimido[2,1-b][1,3]thiazin-6-yl)benzoic acid9 (**9**) (1 mmol) and thionylchloride (1 mL, 13.8 mmol) were refluxed on a steam bath for 6 h. The solvent was evaporated, and then the residue was dissolved in 10 mL of xylene. Thereafter, a moderate stream of N,N-diethylamine (5mmol) and solution of compound **10** were boiled for 4 h. Then, the crude precipitate was filtered off and recrystallized from toluene to give of compound **11**. Yield: 43%, mp 210–211ᵒC. IR (KBr) 1701, 1622, 1574 cm-1 (C=O). 1H-NMR (400 MHz, DMSOd6) δ 7.30-7.00 (m, 14H, Harom.), 6.80 (s, 1H, C4H), 3.81 (m, 4H, CH), 3.40 (bs, 4H, CH2), 1.17 (bs, 6H, CH3). 13C-NMR (100 MHz, DMSOd6) δ 195.8 (C=O, benzoyl), 171.3, 167.1, 164.2 (C=O, C=N), 157.2, 146.3, 135.4, 132.9, 130.9, 130.4, 129.5, 129.0, 128.8, 128.4, 128.0, 127.1, 126.9, 125.4, 124.1, 120.6, 66.8, 43.21, 39.20, 14.11, 12.93 ppm. Anal. Calcd. for C31H29N3O3S: C, 71.10; H, 5.58; N, 8.02. Found: C, 71.11; H, 5.57; N, 8.04.

**RESULTS AND DISCUSSION**

*Synthesis*

In this work, we obtained ethyl 2-(5-benzoyl-4-(3-nitrophenyl)-6-phenyl-3,4-dihydropyrimidin-2(1*H*)-ylidene)acetate (**3**), ethyl 2-(5-benzoyl-4,6-diphenyl-3,4-dihydropyrimidin-2(1*H*)-ylidene)acetate (**4**),4-(6-benzoyl-2-benzylidene-3-oxo-7-phenyl-3,5-dihydro-2*H*-thiazolo[3,2-a]pyrimidin-5-yl)benzoic acid (**6**), 1-(4-(6-benzoyl-3-oxo-7-phenyl-3,5-dihydro-2*H*-thiazolo[3,2-a]pyrimidin-5-yl)benzoyl)-3-phenylurea (**8**) and 4-(7-benzoyl-4-oxo-8-phenyl-2,3,4,6-tetrahydropyrimido[2,1-b][1,3]thiazin-6-yl)-N,N-diethylbenzamide (**11**) compounds.

The synthesis methodology of compounds **3** and **4** are similar to the Eschenmoser sulfide contraction. This reaction yields *β*-enaminocarbonyl derivatives of type IV by the elimination of sulfur from an episulfide intermediate (Scheme 1). This reaction was defined by Knott in 1955 and it was used for the synthesis of [1,3-dicarbonyl compounds](https://en.wikipedia.org/wiki/1,3-dicarbonyl_compound) from a [thioester](https://en.wikipedia.org/wiki/Thioester) by [Albert](https://en.wikipedia.org/wiki/Albert_Eschenmoser) Eschenmoser.10 This method requires a base and a tertiary phosphine. The method has a relevance to [organic chemistry](https://en.wikipedia.org/wiki/Organic_chemistry) and has been notably applied in the [vitamin B12 total synthesis](https://en.wikipedia.org/wiki/Vitamin_B12_total_synthesis).

### 

Scheme 1. The Eschenmoser coupling reaction.

This method generally requires tertiary phosphine but instead of it we used pyridine as a catalyst and synthesized compounds **3** and **4** in a good yield (Scheme 2).

Scheme 2. Synthesis of the compounds **3** and **4**.

The IR spectra of **3** and **4** gave peaks at 3208-3061 cm-1 (NH) and 1622-1594 cm-1 (C=O) groups.

The 1H NMR spectra of the compound **3** showed δ 10.98 (s, 1H, NH), 10.12 (s, 1H, NH), 8.32-7.02 (m, 14H, Harom.), 5.47 (s, 1H, C4H), 5.32 (s, 1H, =CH), 4.45(q, 2H, OCH2), 1.16 (t, 3H, CH3) and the 1H NMR spectra of the compound **4** showed δ 10.96 (s, 1H, NH), 10.11 (s, 1H, NH), 8.30-6.96 (m, 15H, Harom.), 5.44 (s, 1H, C4H), 5.30 (s, 1H, =CH), 4.33 (q, 2H, OCH2), 1.15 (t, 3H, CH3).

When acetic anhydride, α- and β-bromocarboxylic acids were reacted with 4-(5-benzoyl-6-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-4-yl) benzoic acid the reactions resulted 4-(6-benzoyl-3-oxo-7-phenyl-3,5-dihydro-2H-thiazolo[3,2-a]pyrimidin-5-yl)benzoic acid (**5**)9 and 4-(7-benzoyl-4-oxo-8-phenyl-2,3,4,6-tetrahydropyrimido[2,1-b][1,3]thiazin-6-yl)benzoic acid (**9**)9 derivatives, respectively. There are acidic protons at compound **5** (thiazine ring system), so we occurred condensation reaction between thiazine (**5**) and benzaldehyde and obtained compound **6** (Scheme 3).



Scheme 3. Synthesis of the compounds **6**.

On the other hand, after chlorination of compounds **5** and **9** with SOCl2, the reaction of **5** with phenyl urea and the reaction of **9** with N,N-diethylamine were resulted compounds **8** and **11**, respectively (Scheme 4).



Scheme 4. Synthesis of the compounds **8, 11**.

*Calculation analysis*

Full geometry optimizations of the all molecules were performed using DFT based on Beck’s three parameter exchange functional and Lee–Yang–Parr11 nonlocal correlation functional (B3LYP) and the 6-31G (d, p) orbital basis sets in Gaussian09 program5 (Fig. 1).

|  |  |
| --- | --- |
| G:\Serbian esvet ela ahmet\1r\1.tif | G:\Serbian esvet ela ahmet\2r\2.tif |
| **1** | **2** |
| G:\Serbian esvet ela ahmet\3r\3.tif | G:\Serbian esvet ela ahmet\4R\4.tif |
| **3** | **4** |
| **G:\Serbian esvet ela ahmet\5r\5.tif** | **G:\Serbian esvet ela ahmet\6r\6.tif** |
| **5** | **6** |
| **G:\Serbian esvet ela ahmet\7r\7.tif** | **G:\Serbian esvet ela ahmet\8r\8.tif** |
| **7** | **8** |
| **G:\Serbian esvet ela ahmet\9r\9.tif** | **G:\Serbian esvet ela ahmet\10r\10.tif** |
| **9** | **10** |
| **G:\Serbian esvet ela ahmet\11r\11.tif** | |
| **11** | |

Figure 1.Optimizations of all compounds.

Very useful information can be obtained by the quantum chemical calculations to examine the corrosion inhibiting effects of organic compounds. The quantum chemical parameters all compounds such as μ, IP, A, χ, η, w, S, ΔN and ΔEback donation were calculated according to Shojaie. et al. (Tab. 1).

TABLE 1.The quantum chemical parameters for all compounds

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **3** | **4** | **6** | **8** | **11** |
| EHOMO(eV) | -6.8348 | -6.0204 | -0.4212 | -5.7635 | -4.7811 |
| ELUMO(eV) | -3.2312 | -2.0804 | -4.0627 | -2.5709 | -1.7451 |
| Energy gap “∆E” | 3.6036 | 3.9400 | -3.6416 | 3.1925 | 3.0359 |
| Ionization potential “IP(eV)” | 6.8348 | 6.0204 | 0.4212 | 5.7635 | 4.7811 |
| Electron affinity “A(eV)” | 3.2312 | 2.0804 | 4.0627 | 2.5709 | 1.7451 |
| Chemical hardness “η(eV)” | 3.6036 | 3.9400 | -3.6415 | 3.1926 | 3.0360 |
| Chemical softness “S” | 0.2775 | 0.2538 | -0.2746 | 0.3132 | 0.3294 |
| Electronegativity “χ(eV)” | 5.0330 | 4.0504 | 2.2419 | 4.1672 | 3.2631 |
| Transferred electrons fraction “(ΔN)” | 0.2729 | 0.3743 | -0.6533 | 0.4437 | 0.6154 |
| Dipole moment “µ(debye)” | 9.0896 | 3.9613 | 2.6511 | 6.5956 | 3.8746 |
| Electrophilicity index “(ω)” | 11.4636 | 1.9913 | -0.9650 | 6.8129 | 2.4724 |
| ΔE back donation | -0.9009 | -0.985 | 0.9103 | -0.7981 | -0.7590 |

The inhibitory effect of a particular compound is usually attributed to adsorption of the molecule to the metal surface.12 When the chemisorption occurs, one of the species entering the reaction behaves as an electron pair donor and the other acts as an electron pair receiver.

The basic state geometry of the inhibitor and the structure of HOMO and LUMO play a role in the activity properties of the inhibitors. Remarkable, the shape of HOMO and LUMO is structurally dependent (Fig.3). The electron density of the HOMO site in the inhibitors examined is often distributed over atoms with delocalized character, indicating that they are the favorite adsorption domains.

|  |  |  |
| --- | --- | --- |
| **1** | **G:\Serbian esvet ela ahmet\1r\homo.tif** | **G:\Serbian esvet ela ahmet\1r\lumo.tif** |
| **2** | **G:\Serbian esvet ela ahmet\2r\homo.tif** | **G:\Serbian esvet ela ahmet\2r\lumo.tif** |
| **3** | **G:\Serbian esvet ela ahmet\3r\homo.tif** | **G:\Serbian esvet ela ahmet\3r\lumo.tif** |
| **4** | **G:\Serbian esvet ela ahmet\4R\homo.tif** | **G:\Serbian esvet ela ahmet\4R\lumo.tif** |
| **5** | **I:\Serbian esvet ela ahmet\5r\homo.tif** | **I:\Serbian esvet ela ahmet\5r\lumo.tif** |
| **6** | **I:\Serbian esvet ela ahmet\6r\homo.tif** | **I:\Serbian esvet ela ahmet\6r\lumo.tif** |
| **7** | **I:\Serbian esvet ela ahmet\7r\homo.tif** | **I:\Serbian esvet ela ahmet\7r\lumo.tif** |
| **8** | **I:\Serbian esvet ela ahmet\8r\homo.tif** | **I:\Serbian esvet ela ahmet\8r\lumo.tif** |
| **9** | **I:\Serbian esvet ela ahmet\9r\ho.tif** | **I:\Serbian esvet ela ahmet\9r\lu.tif** |
| **10** | **I:\Serbian esvet ela ahmet\10r\ho.tif** | **I:\Serbian esvet ela ahmet\10r\lu.tif** |
| **11** | **I:\Serbian esvet ela ahmet\11r\ho.tif** | **I:\Serbian esvet ela ahmet\11r\lu.tif** |

Figure 2. Schematic representation of HOMO and LUMO molecular orbital of studied molecules.

The inhibitors could not only donate electron metal ions to un-emissive d orbitals, but can also accept electrons from the d-orbital of the metal, which leads to a feedback bond. The electrons found in the HOMO can easily donate. EHOMO also play a most important role during corrosion inhibition course and this is directly related to the ionization potential. Increasing EHOMO leads to higher inhibition effect.13

Another parameter of the molecular structure is the LUMO, which determines the polarisabilities of the compound. The lower the value of ELUMO, the more probable the molecule would accept electrons and the energy of the LUMO is directly related to the electron affinity.14

Similar relations were found between the rates of inhibition and energy gap. Larger values of the energy gap will provide low reactivity to a molecule. Lower values of the energy gap render good inhibition efficiency, because the energy required to remove an electron from the lowest occupied orbital will be low.13,14

Dipole moment (μ Debye) is another important electronic parameter for corrosion inhibitors. The high value of the dipole moment probably increases the adsorption between the chemical compound and the metal surface. 13,14

On the other hand, absolute hardness (η), softness (S), global electrophilicity index (ω) electrons transferred (ΔN), and ΔEback donation values are important properties used to measure the stability and reactivity of a molecule 13,14 (Table 1).

The chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap. 13,14

The global electrophilicity index was introduced by Parr15 as a measure of energy lowering due to maximal electron flow between donor and acceptor this index measures the propensity of chemical species to accept electrons. A good, more reactive, nucleophile is characterized by lower value of µ, ω; and conversely a good electrophile is characterized by a high value of µ, ω. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ∆N from the environment. Thus the fraction of electrons transferred from the inhibitor to metallic surface.

According to the simple charge transfer model for donation and back-donation of chargesan electronic back-donation process might be occurring governing the interaction between the inhibitor molecule and the metal surface. The concept establishes that if both processes occur, namely charge transfer to the molecule and back-donation from the molecule, the energy change is directly proportional to the hardness of the molecule.16-19

The ∆Eback donation implies that when η > 0 and ∆Eback donation <0 the charge transfer to a molecule, followed by a back donation from the molecule, is energetically favored. In this context, hence, it is possible to compare the stabilization among inhibiting molecules, since there will be an interaction with the same metal, then, it is expected that it will decrease as the hardness increases. 16-19

According to the calculations, the compound **6** appears to be a good inhibitor for corrosion.

*Molecular electrostatic potentials (MEP)*

The MEP was run at B3LYP / 6-31G (d, p) for molecule **6**. The MEP provides information about reactive sites for electrophilic and nucleophilic attack as well as hydrogen-bonding interactions in molecules. We studied the MEP for molecule **6** given in Fig. 5. The electrostatic potentials at the surface are represented by different colors; red, blue and green represent the regions of negative, positive and zero electrostatic potential respectively. In addition, the negative regions (red color) of MEP are related to electrophilic reactivity, and the positive regions (blue color) are related to the nucleophilic reactivity.

|  |  |  |  |
| --- | --- | --- | --- |
|  | G:\Serbian esvet ela ahmet\6r\map1.tif | G:\Serbian esvet ela ahmet\6r\map 2.tif | G:\Serbian esvet ela ahmet\6r\map 3.tif |

Figure 3. The molecular electrostatic potentials maps for compound **6**.

**CONCLUSION**

The pyrimidine derivatives were synthesized and all structures determined by using FT-IR, 1H/13C NMR and elemental analyses. The compounds were investigated as corrosion inhibitors using density functional theory (DFT) at the level of B3LYP/6-31G (d, p).

As presented in Table 1, the compound which have the lowest energetic gap is the compound **6** (∆E = -3.6416 eV). This lower gap allows it to be the softest molecule. The compound that has the highest HOMO energy is the compound **6** (EHOMO = -0.4212 eV). This higher energy allows it to be the best electron donor.

The two properties like I (potential ionization) and A (affinity) are so important, the determination of these two properties allow us to calculate the absolute electro negativity (χ) and the absolute hardness (η). These two parameters are related to the one-electron orbital energies of the HOMO and LUMO respectively. Compound **6** has lowest value of the potential ionization (I =0.4212 eV), so that will be the better electron donor. Compound **6** has the largest value of the affinity (A = 4.0627 eV), so it is the better electron acceptor. The chemical reactivity varies with the structural of molecules.

Chemical hardness (softness) value of compound **6** (η = -3.6415 eV, S = -0.2746 eV) is lesser (greater) among all the molecules. Thus, compound **6** is found to be more reactive than all the compounds. Compound **6** possesses lowest electro negativity value (χ = 2.2419 eV) than all compounds so; it is the best electron donor. The value of ω for compound **6** (ω = -0.9650 eV) indicates that it is the stronger nucleophile than all other compounds.

According to all of the calculations, the compound **6** appears to be a good inhibitor for corrosion then other molecules.

**REFERENCES**

1. K. Rasheeda, V. D. P. Alva, P. A. Krishnaprasad and S. Samshuddin, *Int. J. Corros. Scale Inhib.* **7** (2018) 48. (<http://dx.doi.org/10.17675/2305-6894-2018-7-1-5>)

2. [S. Samshuddin](https://www.ncbi.nlm.nih.gov/pubmed/?term=Samshuddin%20S%5BAuthor%5D&cauthor=true&cauthor_uid=23468785), [B. Narayana](https://www.ncbi.nlm.nih.gov/pubmed/?term=Narayana%20B%5BAuthor%5D&cauthor=true&cauthor_uid=23468785), [H. S. Yathirajan](https://www.ncbi.nlm.nih.gov/pubmed/?term=Yathirajan%20HS%5BAuthor%5D&cauthor=true&cauthor_uid=23468785), [T. Gerber](https://www.ncbi.nlm.nih.gov/pubmed/?term=Gerber%20T%5BAuthor%5D&cauthor=true&cauthor_uid=23468785), [E. Hosten](https://www.ncbi.nlm.nih.gov/pubmed/?term=Hosten%20E%5BAuthor%5D&cauthor=true&cauthor_uid=23468785), and [R. Betz](https://www.ncbi.nlm.nih.gov/pubmed/?term=Betz%20R%5BAuthor%5D&cauthor=true&cauthor_uid=23468785)*,* [*Acta Crystallogr Sect E Struct Rep Online*](https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3588820/)*.* **68** (12) (2012) 3271. (<https://doi.org/10.1107/S1600536812044662>)

# 3.Yu.I. Kapustin, A.G. Kholodkova and T.A. Vagramyan*,* *[Internatıonal Journal Of Corrosıon And Scale Inhıbıtıon](http://ijcsi.pro/),* 7(1) (2018) 1, (<http://dx.doi.org/10.17675/2305-6894-2018-7-1-1>)

4. a- E. Akbas, A. Ruzgar, E. Sahin and E. Ergan, [Journal of Heterocyclic Chemistry](https://onlinelibrary.wiley.com/journal/19435193), **3** (2019) 1003. (<https://doi.org/10.1002/jhet.3483>); b- E. Akbas, E. Ergan, E. Sahin, S. Ekin, M. Cakir and Y. Karakus, *Phosphorus, Sulfur, And Sılıcon And The Related Elements. (*https://doi.org/10.1080/10426507.2018.1550489).

5. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R.Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M.Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J.A. Montgomery, J.E. Peralta, F.Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R.Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J.Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V.Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J.Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö.Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, 2009. Gaussian 09, Revision D. 01. Gaussian Inc. Wallingford CT. (<https://doi.org/10.1159/000348293>)

6. a- G. Gece, *Materials and Corrosion* **64** (10) (2013) 940 <https://doi.org/10.1002/maco.201106482>; b- F. Shojaie, N. M.Baghini, *Int J Ind Chem.,* **6** (2015) 297, (<https://doi.org/10.1007/s40090-015-0052-x>)

7. E. Akbas, F. Aslanoglu, B. Anil and A. Sener, *J. Heterocyclic Chem.,* **45** (2008) 1457. (<https://doi.org/10.1002/jhet.5570450532>)

8. E. Akbas and F. Aslanoglu, *Phosphorus, Sulfur, and Silicon*, **183** (2008) 82. (<https://doi.org/10.1080/10426500701557021>)

9. E. Akbas, A. Erdogan, E. Ergan, M. Gulcan and A. Ruzgar, *J. Chem. Soc. Pak.,* **39** (2) (2017) 269. (<https://doi.org/10.1007/s12039-019-1602-0>)

10. A. Eschenmoser and C. E. Wintner, *Science,* **196** (1977) 1410. (<https://doi.org/10.1126/science.867037>)

11. C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B.* **37** (1988) 785. (<https://doi.org/10.1103/PhysRevB.37.785>)

12. [S. A. X. Stango](https://www.tandfonline.com/author/Xavier+Stango%2C+S+Arul), [U. Vijayalakshmi](https://www.tandfonline.com/author/Vijayalakshmi%2C+U), [*Journal of Asian Ceramic Societies*,](https://www.tandfonline.com/toc/tace20/current)6 (2018) 20, (<https://doi.org/10.1080/21870764.2018.1439608>)

13. G. Gece, *Corrosion Science,* **50** (2008) 2981. (<https://doi.org/10.1016/j.corsci.2008.08.043>)

14. A. Popova, M. Christov, A. Zwetanova, *Corrosion Science*, **49** (2007) 2131. (<https://doi.org/10.1016/j.corsci.2006.10.021>)

15. R. G. Parr and L. Szentpaly, *J. Am. Chem. Soc.* **121** (1999) 1922. (<https://pubs.acs.org/doi/10.1021/ja983494x>)

16. P. K. Chattaraj, U. Sarkar and D. R. Roy, *Electrophilicity Index Chem. Rev.* **106** (2006) 2065. (<https://doi.org/10.1021/cr040109f>)

17. C. Farley, N.V.S.D.K. Bhupathiraju, B.K. John, C.M. Drain, *J. Phys. Chem. A* **120** (2016)7451. (<https://pubs.acs.org/doi/10.1021/acs.jpca.6b07024>)

18. A. D. Becke, J. Chem. Phys. **96** (1992) 2155. (<https://doi.org/10.1063/1.462066>)

19. A. D. Becke, J. Chem. Phys. **98** (1993) 5648. (<https://doi.org/10.1063/1.464913>)