Synthesis, characterization, quantum chemical studies and electrochemical performance of new 4,7-dihydropyrimidino[1,5-a]pyrimidine derivatives

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Abstract. In this study, 4,7-dihydropyrimidino[1,5-a]pyrimidine derivatives (**1–5**) were prepared *via* Multicomponent Cyclocondensation Reactions (MCRs). All structures were 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). According to the calculations, compound **1** appears to be a good inhibitor for corrosion. In addition, the electrochemical properties of the novel systems were investigated by CV.

Keywords. Pyrimidine; DFT; MCRs; quantum chemical studies; electrochemistry.

1. Introduction

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. Several 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 the metal surface.¹ However, the use of several heterocyclic inhibitors has caused negative effects on the environment because of their toxicity and non-biodegradability. In this context, pyrimidine derivatives are found to attract great interest due to their environmentally benign properties.²

The chemistry of pyrimidine derivatives plays an important role in the field of 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.³ 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.⁴ 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 an essential part in many natural products such as nucleic bases, vitamins, enzymes, chlorophyll, haemoglobin and hormones.⁴ 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 the 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 fulfilled by pyrimidine molecule.

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Scheme 1. Biginelli three-component cyclocondensation reaction.

Hence, pyrimidine derivatives are expected to be excellent corrosion inhibitors at the industrial level, not only due to their efficiency but also due to their non-toxic nature.³

Various methods have been reported in the literature for the synthesis of pyrimidine derivatives. One of these is the Biginelli reaction.⁵ The Biginelli reaction is very simple one-pot, acid catalyzed cyclocondensation reaction of benzaldehyde, urea and ethyl acetoacetate (Scheme 1).

In this work, we synthesized novel (7-(4-methoxy-3-methylphenyl)-5-phenyl-4,7-dihydro-1,5-a) pyrimidin-6-yl(phenyl)methanone (**1**), (7-(4-methoxyphenyl)-5-phenyl-4,7-dihydro-1,5-a) pyrimidin-6-yl(phenyl)methanone (**2**), (5,7-diphenyl-4,7-dihydro-1,5-a) pyrimidin-6-yl(phenyl)methanone (**3**), (7-(4-(dimethylamino)phenyl)-5-phenyl-4,7-dihydro-1,5-a) pyrimidin-6-yl(phenyl)methanone (**4**) and phenyl (5-phenyl-7-(4-(trifluoromethyl)phenyl)-4,7-dihydro-1,5-a) pyrimidin-6-yl)methanone (**5**) in light of the Biginelli reaction.

The quantum chemical calculations (QCCs) have been widely used in the reactivity of organic compounds for corrosion inhibition. In this work, the theoretical calculations for the inhibition potentials were explained using QCCs based on DFT.⁶ First, the E_{HOMO} and E_{LUMO} energies of the molecules were calculated in the Gaussian. The high E_{HOMO} value has a compound 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 the energy gap (ΔE). Larger values of ΔE 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.⁷⁻⁹ 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 Karzazi *et al.*

On the other hand, the electrochemical properties of the synthesized compounds were investigated by CV.

2. Experimental

2.1 Materials and methods

Melting points: Electrothermal Gallenkamp; Microanalyses: LECO CHNS 932 Elemental Analyzer; FT-IR: Mattson 1000 (KBr); ^1H and ^{13}C NMR: Varian Mercury 300 MHz (TMS); TLC: DC Alufolien Kieselgel 60 F 254 Merck, Camag lamp (254/365 nm). Electrochemical experiments were performed with an Autolab PGSTAT 128N potentiostat, (The Netherlands) using a three electrode system, glassy carbon working electrode (Φ : 3 mm, BAS), a platinum wire as an auxiliary electrode and Ag/AgCl (NaCl 3M, Model RE-1, BAS, USA) as a reference electrode. Before starting each experiment, the glassy carbon electrode was polished manually with alumina (Φ : 0.01 μm). Cyclic voltammetric (CV) experiments were recorded at room temperature in extra pure DMSO, and ionic strength was maintained at 0.05 mol L^{-1} with electrochemical grade tetraethylammonium tetrafluoroborate (TEATFB) as the supporting electrolyte. Solutions were deoxygenated by a stream of high purity nitrogen for 15 min prior to the experiments, and during the experiments, nitrogen flow was maintained over the solution.¹⁰

2.2 Synthesis

2.2a (7-(4-Methoxy-3-methylphenyl)-5-phenyl-4,7-dihydro-1,5-a) pyrimidin-6-yl(phenyl)methanone (1**):** The dibenzoyl methane (1 mmol), 5-aminotetrazol (1 mmol) and 4-methoxy-3-methylbenzaldehyde (1 mmol) boiled in CH_3COOH (10 mL) with a few drops concentrated HCl for 8 h and monitored by TLC. The resulting mixture was cooled to room temperature, washed with water and recrystallized from methanol (85%) to give pure product **1** (Scheme 2).

Other synthesized pyrimidine compounds (**2–5**) were obtained by similar procedure using different aromatic aldehydes.

M.p. 263–264 $^{\circ}\text{C}$; IR (potassium bromide): 3214, 2947, 1687, 1650, 1588, 1559 cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$): δ 11.96 (s, 1H, NH), 7.35–6.80 (m, 13H, $\text{H}_{\text{arom.}}$), 6.64 (s, 1H, CH), 3.84 (s, 3H, OCH_3), 2.15 (s, 3H, CH_3). ^{13}C NMR ($\text{DMSO}-d_6$): 194.82 (benzoyl), 169.50, 157.78, 149.55, 144.67,

Scheme 2. Synthesis of compound 1.

139.19, 133.90, 131.98, 130.14, 130.12, 129.10, 128.71, 128.42, 127.94, 126.93, 126.24, 110.64, 108.08, 60.60, 55.68, 16.42. Anal. Calcd. for $C_{25}H_{21}N_5O_2$: C, 70.91; H, 5.00; N, 16.54, Found: C, 70.90; H, 5.08; N, 16.50.

2.2b (7-(4-Methoxyphenyl)-5-phenyl-4,7-dihydro-1H-tetrazolo[1,5-a]pyrimidin-6-yl)(phenyl) methanone (**2**): The crude product was recrystallized from ethanol. Yield 83%, M.p. 268–270 °C; IR (potassium bromide): 3217, 2966, 1695, 1627, 1587, 1546 cm^{-1} ; 1H NMR (DMSO- d_6): δ 11.94 (s, 1H, NH), 7.41–7.00 (m, 14H, $H_{arom.}$), 6.87 (s, 1H, CH), 2.50 (s, 3H, OCH_3). ^{13}C NMR (DMSO- d_6): 194.41 (benzoyl), 169.10, 159.24, 149.66, 149.13, 144.40, 138.70, 133.34, 131.29, 131.27, 129.94, 128.89, 127.96, 114.00, 107.60, 60.00, 55.04, 28.69. Anal. Calcd. for $C_{24}H_{19}N_5O_2$: C, 70.40; H, 4.68; N, 17.10, Found: C, 70.45; H, 4.70; N, 17.08.

2.2c (5,7-Diphenyl-4,7-dihydro-1H-tetrazolo[1,5-a]pyrimidin-6-yl)(phenyl)methanone (**3**): The crude product was recrystallized from ethanol. Yield 79%, M.p. 257–262 °C; IR (potassium bromide): 3217, 2972, 1695, 1629, 1587, 1548 cm^{-1} ; 1H NMR (DMSO- d_6): δ 11.97 (s, 1H, NH), 7.48–7.01 (m, 15H, $H_{arom.}$), 6.93 (s, 1H, CH). ^{13}C NMR (DMSO- d_6): 194.39 (benzoyl), 169.11, 149.61, 149.21, 144.16, 139.82, 138.71, 133.27, 131.25, 130.00, 129.65, 128.73, 128.26, 127.97, 127.54, 107.41, 60.36. Anal. Calcd. for $C_{23}H_{17}N_5O$: C, 72.81; H, 4.52; N, 18.46, Found: C, 72.80; H, 4.55; N, 18.42.

2.2d (7-(4-(Dimethylamino)phenyl)-5-phenyl-4,7-dihydro-1H-tetrazolo[1,5-a]pyrimidin-6-yl)(phenyl) methanone (**4**): The crude product was recrystallized from toluene. Yield 86%, M.p. 250–251 °C; IR (potassium

bromide): 3216, 3086, 2944, 1692, 1627, 1582, 1550 cm^{-1} ; 1H NMR (DMSO- d_6): δ 11.94 (s, 1H, NH), 7.75–6.94 (m, 14H, $H_{arom.}$), 6.44 (s, 1H, CH), 2.82 (s, 6H, CH_3). ^{13}C NMR (DMSO- d_6): 194.40 (benzoyl), 165.02, 149.61, 144.44, 139.21, 131.71, 130.43, 130.32, 130.18, 130.08, 129.09, 128.76, 127.97, 127.69, 112.43, 107.87, 60.67, 46.69. Anal. Calcd. for $C_{25}H_{22}N_6O$: C, 71.07; H, 5.25; N, 19.89, Found: C, 71.01; H, 5.28; N, 19.91.

2.2e Phenyl (5-phenyl-7-(4-(trifluoromethyl)phenyl)-4,7-dihydro-1H-tetrazolo[1,5-a]pyrimidin-6-yl) methanone (**5**): The crude product was recrystallized from ethanol. Yield 76%, M.p. 262–265 °C; IR (potassium bromide): 3217, 2945, 1695, 1629, 1585, 1548 cm^{-1} ; 1H NMR (DMSO- d_6): δ 11.96 (s, 1H, NH), 7.74–6.98 (m, 14H, $H_{arom.}$), 6.44 (s, 1H, CH). ^{13}C NMR (DMSO- d_6): 194.36 (benzoyl), 169.10, 149.66, 149.13, 145.94, 144.40, 138.70, 133.34, 131.29, 131.27, 129.94, 128.89, 127.96, 125.69, 122.09, 106.65, 59.93, 22.68. Anal. Calcd. for $C_{24}H_{16}F_3N_5O$: C, 64.43; H, 3.60; N, 15.65, Found: C, 64.45; H, 3.64; N, 15.62.

2.3 Electrochemical analysis

Electrochemical properties of the present compounds were carried out by CV technique on glassy carbon electrode surface in 0.005 M TEATFB/DMSO medium. Electrochemical measurements were taken in the cathodic direction from –1.2 V to +1.8 V. The obtained data are given in Table 1.

3. Results and Discussion

3.1 Synthesis

In this work, we obtained (7-(4-methoxy-3-methylphenyl)-5-phenyl-4,7-dihydro-1H-tetrazolo[1,5-a]pyrimidin-6-yl)(phenyl) methanone (**1**), (7-(4-methoxyphenyl)-5-phenyl-4,7-dihydro-1H-tetrazolo[1,5-a]pyrimidin-6-yl)(phenyl) methanone (**2**), (5,7-diphenyl-4,7-dihydro-1H-tetrazolo[1,5-a]pyrimidin-6-yl)(phenyl)methanone (**3**), (7-(4-(dimethylamino)phenyl)-5-phenyl-4,7-dihydro-1H-tetrazolo[1,5-a]pyrimidin-6-yl)(phenyl) methanone (**4**) and phenyl (5-phenyl-7-(4-(trifluoromethyl)phenyl)-4,7-dihydro-1H-tetrazolo[1,5-a]pyrimidin-6-yl) methanone

Table 1. Voltammetric results at a scan rate of 100 mVs $^{-1}$ vs. Ag/AgCl. Ec: cathodic, Ea: anodic.

Compound	Ec (V)	Ea (V)
1	Ic: +0.26, IVc = –1.39	Ia: +0.09, IIa $^{-}$: +0.78, IVa = –1.22
2	Ic: +0.18, IVc = –1.35	Ia: +0.13, IIa $^{-}$: +0.82, IVa = –1.20
3	Ic: +0.23, IVc = –1.37	Ia: +0.18, IIa $^{-}$: +0.81, IVa = –1.20
4	Ic: +0.34, IIc: –0.87, IIIc: –1.15, IVc = –1.38	Ia: +0.34, IIa $^{-}$: +1.04, IVa = –1.11
5	Ic: +0.23, IVc: –1.33	Ia: +0.14, IIa $^{-}$: +0.83, IVa = –1.20

Scheme 3. Synthesis of compounds 1–5.

Figure 1. ¹H NMR spectra of the compound 1.

(5) compounds *via* the Biginelli reaction in good yields (Scheme 3).

The IR spectra of **1** gave peaks at 3217 cm⁻¹(NH), 2947 cm⁻¹(CH), 1687 cm⁻¹(C = O), 1650, 1588, 1559 cm⁻¹ (N = N), (C = N) and (C = C) groups.

The ¹H NMR spectra of compound **1** showed δ 11.97 (s, 1H, NH), 7.35–6.80 (m, 13H, H_{arom.}), 6.64 (s, 1H, CH), 3.84(s, 3H, OCH₃) and 2.35(s, 3H, CH₃) (Figure 1).

The IR spectra of **2** showed at 3217 cm⁻¹ (NH), 2947 cm⁻¹(CH), 1687 cm⁻¹ (C = O), 1650, 1588, 1559 cm⁻¹ (N = N), (C = N) and (C = C) groups. The ¹H NMR spectra of the compound **2** showed δ 11.94 (s, 1H, NH), 7.41–7.00 (m, 14H, H_{arom.}), 6.87 (s, 1H, CH), 2.50 and 2.35(s, 3H, CH₃). In the ¹H-NMR spectra of compound **3** exhibited singlet signal at δ 11.97 NH, multiplet signals at 7.48–7.01 aromatic and singlet signal at 6.93 C4H protons. Singlet signal at δ 11.94 NH, multiplet signals at 7.75–6.94 aromatic, singlet signal at 6.44 C4H and singlet signal at 2.82 2CH₃ were observed for compound **4** protons. On the other hand in the ¹H-NMR spectra of compound **5** appeared singlet signal at δ 11.96 NH,

multiplet signals at 7.74–6.98 aromatic and singlet signal at 6.44 CH protons.

3.2 Calculation analysis

Full geometry optimizations of all molecules were performed using DFT based on Beck's three parameter exchange functional and Lee–Yang–Parr nonlocal correlation functional (B3LYP)^{11–13} and the 6-31G (d, p) orbital basis sets in Gaussian09 program¹⁴ (Figure 2).

Very useful information can be obtained by this method to examine the corrosion inhibiting effects of organic compounds. The quantum chemical parameters all compounds such as μ, I, A, χ, η, w, S, ΔN and ΔE_{back donation} were calculated according to Karzazi *et al.* (Table 2).

The inhibitory effect of a particular compound is usually attributed to adsorption of the molecule to the metal surface.¹⁵ 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 (Figure 3).

Figure 2. Optimizations of all compounds.

Table 2. The quantum chemical parameters for all compounds.

	1	2	3	4	5
$E_{\text{HOMO}}(\text{eV})$	−5.7488	−6.0111	−6.1793	−5.2484	−6.4392
$E_{\text{LUMO}}(\text{eV})$	−3.7955	−1.8463	−1.9146	−1.7348	−2.1653
Energy gap “ ΔE ”	1.9533	4.1648	4.2647	3.5136	4.2739
Ionization potential “ $I(\text{eV})$ ”	5.7488	6.0111	6.1793	5.2484	6.4392
Electron affinity “ $A(\text{eV})$ ”	3.7955	1.8463	1.9146	1.7348	2.1653
Chemical hardness “ $\eta(\text{eV})$ ”	1.9533	4.1648	4.2647	3.5136	4.2739
Chemical softness “ S ”	0.5119	0.2401	0.2345	0.2846	0.2339
Electronegativity “ $\chi(\text{eV})$ ”	4.7722	3.9287	4.0469	3.4916	3.9573
Transferred electrons fraction “ (ΔN) ”	0.5703	0.3687	0.3462	0.4992	0.3559
Electrophilicity index “ (ω) ”	1.8717	2.0465	1.6138	3.7476	9.4278
Dipole moment “ $\mu(\text{debye})$ ”	2.7041	4.1287	3.7101	5.1318	8.9769
$\Delta E_{\text{back donation}}$	−0.4883	−1.0412	−1.0662	−0.8784	−1.0685

The basic state geometry of the inhibitor and the structure of HOMO and LUMO play a role in the activity properties of the inhibitors. Remarkably, the shape of HOMO and LUMO is structurally dependent (Figure 4). 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.

When HOMO and LUMO are compared, it is seen that all inhibitors have delocalization and tautomerization between benzoyl and NH group (Scheme 4).

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 E_{LUMO} shows the molecule's ability to accept electrons. With an increase

Figure 3. Interaction of inhibitor and metal.

in HOMO, the inhibitor's ability to bond to the metal surface increases and decreases with lower LUMO energy values. Therefore, the lower E_{LUMO} value is more likely as a molecule to accept electrons.

According to the obtained data, it can be said that compound **1** ($E_{\text{LUMO}} -3.7955\text{eV}$) will show the best inhibitory effect.

Figure 4. Schematic representation of HOMO and LUMO molecular orbital of studied molecules.

Scheme 4. The delocalization and tautomerization.

The energy gap (ΔE) is an important parameter as a function of the reactivity of the inhibitor molecule towards adsorption on the metal surface. Lower values of ΔE difference will provide good inhibition.^{16,17} A molecule with a low ΔE is more polarized and is usually associated with high chemical activity and low kinetic stability and is called a soft molecule.¹⁸ In this study, ΔE values are among $5 > 3 > 2 > 4 > 1$. The result shows that molecule **1** could perform better as a corrosion inhibitor (Table 2).

The experimental studies on the corrosion inhibition effect of the pyrimidine compounds were present as cationic species in acidic solutions.¹⁹ Schematic representation of studied new synthesized pyrimidine compounds belongs to the mechanism of inhibition demonstrated in Scheme 5.

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.²⁰ Compound **1** will be the best performing inhibitor with a value of 2.7041_{Debye} (Table 2).

Absolute hardness (η) and softness (S) are important properties used to measure the stability and reactivity

of a molecule.^{20,21} The compound **1** with values of the $\eta = 1.9533$ and softness $S = 0.5119$ eV will show the highest inhibition effect.

The electrons transferred (ΔN) values were also calculated (Table 1). When the value of $\Delta N < 3.6$, inhibition efficiency increases.^{21,23} It will be seen that compound **1** (0.5703) will have the best inhibition effect when the ΔN values of the compounds are compared.

The global electrophilicity index (ω) and the $\Delta E_{\text{back donation}}$ values for the compounds demonstrate that molecule **1** exhibit a good inhibitory effect (Table 2).

3.3 Molecular electrostatic potentials (MEP)

The MEP was run at B3LYP/6-31G (d, p) for molecule **1**. 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 **1** given in Figure 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.

3.4 Electrochemistry

Electrochemical properties of the present compounds were carried out by CV technique on the glassy carbon electrode. As can be clearly seen from Figure 6,

Scheme 5. Possible corrosion mechanism in the acidic environment.

Figure 5. The molecular electrostatic potentials maps for compound **1**.

Figure 6. Cyclic voltammogram of compounds (1 mM) at 100 mVs^{-1} scan rate on glassy carbon electrode in TEATFB/DMSO. (6): 0.005 M support electrolyte TEATFB/DMSO. Insert: reduced format.

it is seen that all compounds give a non-sensitive reduction wave (Ic) at about $+0.26 \pm 0.08 \text{ V}$. It is clear that all compounds give a highly sensitive reduction peak (IVc) at about $+1.36 \pm 0.03 \text{ V}$. When scanning was continued on the anodic direction, IVa oxidation peak

was observed in all compounds at about -1.20 V . It is also observed that a non-sensitive and broad Ia oxidation peak occurs at about $+0.22 \pm 0.11 \text{ V}$. The most striking aspect of this study the compounds **1**, **2**, **3** and **5** showed a sensitive oxidation peak at about $+0.80 \pm 0.03 \text{ V}$ (II'a), while the **4** compounds were oxidized at about $+1.04 \text{ V}$ (II'a). Moreover, when investigated in detail in Figure 6, other compounds with the except of **4** are shown to be oxidized/reduced in similar regions. Also, another important difference is the reduction peaks (IIc and IIIc) observed at about -0.87 V and -1.15 V , respectively.

The effects of scanning rate ($25\text{--}500 \text{ mV/s}$) on the peak potential and current intensity were investigated (Figure 7). Calculations were made over this reduction peak because the reductions of IVc in all compounds are more sensitive and stable. In all compounds, the peak potential shifts towards negative when the scanning rate increases. It is seen that there is a linear relationship between scanning rate and peak current in order for **1**, **2**, **3**, **4** and **5**: ($i_p (\mu\text{A}) = 63.25 v (\text{Vs}^{-1}) - 2.34, r = 0.978$, $i_p (\mu\text{A}) = 68.78 v (\text{Vs}^{-1}) + 6.11, r = 0.968$, $i_p (\mu\text{A}) = 85.52 v (\text{Vs}^{-1}) + 7.15, r = 0.967$, $i_p (\mu\text{A}) = 72.12 v (\text{Vs}^{-1}) + 1.43, r = 0.938$ and $i_p (\mu\text{A}) = 69.21 v (\text{Vs}^{-1}) - 6.79, r = 0.981$. Furthermore, it can be said that the diffusions under the

Figure 7. Cyclic voltammograms of compounds (1 mM) at on glassy carbon electrode in TEATFB/DMSO at various scan rates.

effect of adsorption of the electrochemical oxidation reaction of the compounds whose slopes are close to 0.5 are also effective, from the relationship between the logarithm of the peak current and the logarithm of the scan rate, **1**; $\log i_p (\mu\text{A}) = 0.493 \log v + 1.245$, $r = 0.887$, **2**; $\log i_p (\mu\text{A}) = 0.502 \log v - 6.08$, $r = 0.896$, **5**; $\log i_p (\mu\text{A}) = 0.485 \log v + 4.23$, $r = 0.871$, **4**; $\log i_p (\mu\text{A}) = 0.491 \log v + 8.19$, $r = 0.921$ and **1**; $\log i_p (\mu\text{A}) = 0.501 \log v + 4.105$, $r = 0.971$.

In each series of compounds, the cathodic or anodic peak potential corresponding to the intramolecular reductive coupling of the imine and carbonyl groups varies as can be expected from the electronic effects of the substituents attached to the phenyl bounded at position 4 of the dihydropyrimidine ring system. Thus, in the present case, the cathodic and anodic peak potentials become more negative according to the sequence CH_3 , OCH_3 , Ph and CF_3 , in order of a decrease in both electron-withdrawing and acceptor qualities of the substituents. On the other hand, the location of an electron donating $\text{N}(\text{CH}_3)_2$ group on the phenyl connected to C4 results in even much negative electron potentials. This difference indicates that the reduction event is easier with the effect of the amine group in compound **4** and that two different the reduction peaks (IIc and IIc) occur. This agrees with a mechanism for the electrochemical reduction of the pyrimidines in the present study.

4. Conclusions

The newly 4,7-dihydrotetrazolo[1, 5-*a*]pyrimidine derivatives were synthesized *via* Biginelli reaction. All structures were determined by using FT-IR, $^1\text{H}/^{13}\text{C}$ 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). According to the calculations, compound **1** appears to be a good inhibitor for corrosion. The electrochemical analysis of the present systems showed that the electronic effects of the substituents attached to the phenyl bounded at position 4 of the dihydropyrimidine ring system has a quite important role in the cathodic and anodic peak potential corresponding to the intramolecular reductive coupling of the imine and carbonyl groups as expected. The data revealed that more the electronegative the group attached to the phenyl moiety, the more negative the cathodic and anodic peak potentials are. In addition, these compounds may be used as sensors and electrode modification agents in electrochemical studies.

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