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# Synthesis of new 1, 2, 4-triazole derivatives and their anticorrosion properties on mild steel in hydrochloric acid medium

Doddahosur M. Gurudatt [a], Kikkeri N. Mohana [a,*], Harmesh C. Tandon [b]

[a] Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, Karnataka, India
[b] Department of Chemistry, Sri Venkateswara College, Dhula Kuan, New Delhi 110021, India

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ABSTRACT

New 1, 2, 4-triazole derivatives have been synthesized and their anticorrosion properties established. The structures of these compounds were confirmed by spectral studies. The corrosion inhibition of mild steel in 0.5 M HCl by the three derivatives at 0.01–0.05 g $L^{-1}$ was studied using mass loss and electrochemical techniques. Corrosion inhibition mechanism was proposed based on activation and adsorption thermodynamic parameters. Scanning electron microscopy exhibited the film formed on the metal surface. The electronic properties of the inhibitors were obtained from Hyperchem 7.5 package program. Excellent correlation was found between theoretical and experimental results.



## 1. Introduction

The study of carbon steel corrosion phenomenon has become an important industrial and academic topic, especially in acid media [1] due to increased industrial applications of acidic solutions. Acids are being used in acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and in petrochemical processes. Aqueous solutions of acids are the powerful corrosive medium. Hence, the rate of corrosion at which metals are destroyed under acidic medium is very high, especially when soluble corrosion products are formed. Corrosion inhibitors are of great practical importance, being extensively employed in minimizing the metallic waste in engineering materials [2]. Therefore, exploration and investigation of corrosion inhibitor for steel in acid solutions is of prime importance not only from academic point but also for practical applications [3]. The study of materials corrosion processes and their inhibition by organic inhibitors is one of the active fields of research [4]. Most of the efficient inhibitors are organic compounds which mainly contain oxygen, sulfur and nitrogen atoms and multiple bonds in the molecule through which they get adsorbed on to the metal surface. The effectiveness of adsorption mainly depends on the nature and surface charge of the metal, the corroding medium and the inhibitor molecule chemical structure such as functional groups, aromaticity π-orbital character of the donating electron, steric factor and electron density of the donor atoms [5].

The importance of triazolopyrimidines is well recognized in synthetic chemistry because these heterocycles have structures similar to that of purine and adenine, and their fused ring system having differing pyrimidine nitrogen atom in a bridgehead position [6]. Organic compounds in recent decades, including triazole derivatives [7], tetrazole derivatives [8], thiadiazole derivatives [9], cysteine [10], substituted uracils [11], and imidazole derivatives [12] were proved as excellent corrosion inhibitors in acid media. Triazole and triazole-type compounds containing nitrogen and sulfur have attracted more attention because of their excellent corrosion inhibition performance [13]. New triazole derivatives have been continuously synthesized and investigated as inhibitors of metal corrosion in acidic solutions [14]. The triazole derivatives have special affinity towards metal surface displacing water molecules on the surface. In addition, they possess abundant π-electrons and unshared electron pairs on the nitrogen atom that can interact with d-orbitals of iron to provide a protective film.

In the present work, attempt was made to synthesize and to characterize triazole derivatives and test their anticorrosion performance on mild steel in acid medium. The corrosion inhibition performance evaluated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The experimental findings were discussed with various activation and adsorption thermodynamic parameters. The protective film formed on the metal surface was characterized by SEM. Inhibition mechanism of 1,2,4-triazole derivatives was proposed and correlated with the corrosion inhibition efficiency. The experimental findings were correlated with quantum chemical calculations.

* Corresponding author.
*E-mail address:* drknmohana@gmail.com (K.N. Mohana).

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## 2. Experimental

### 2.1. Materials and methods

All solvents and reagents were purchased from Sigma Aldrich Chemicals Pvt Ltd. Melting range was determined by Veego Melting Point VMP III apparatus. Elemental analyses were recorded on Vario MICRO Superuser V1.3.2 Elementar. The FT-IR spectra were recorded using KBr disks on FT-IR Jasco 4100 infrared spectrophotometer. $^1$H NMR spectra were recorded on Bruker DRX −500 spectrometer at 400 MHz using $d_6$-DMSO as solvent and TMS as an internal standard. $^{13}$C NMR spectra was recorded at 100 MHz Bruker DRX 500 spectrometer using $d_6$-DMSO as solvent and TMS as internal standard. The mass spectra of the samples were recorded using LC-MSD-Trap-XCT. Silica gel column chromatography was performed using Merck 7734 silica gel (60–120 mesh) and Merck-made TLC plates.

Mild steel (MS) used in the present study having the following chemical composition (in wt.%): C — 0.051; Mn — 0.179; Si — 0.006; P — 0.005; S — 0.023; Cr — 0.051; Ni — 0.05; Mo — 0.013; Ti — 0.004; Al — 0.103; Cu — 0.050; Sn — 0.004; B — 0.00105; Co — 0.017; Nb — 0.012; Pb — 0.001 and the remainder is iron. Prior to gravimetric and electrochemical measurements, the surface of the specimens was polished under running tap water using SiC emery paper up to 1200 grade, rinsed with distilled water, dried on a clean tissue paper, immersed in benzene for 5 s, dried and then immersed in acetone for 5 s and dried with clean tissue paper. Finally, the specimens were kept in desiccator until use. At the end of the test, the specimens were carefully washed with benzene and acetone, dried and then weighed. Appropriate concentrations of acid were prepared using double distilled water.

### 2.2. Synthesis of inhibitors

#### 2.2.1. Synthesis of 1-(5-bromo-2-chloropyrimidine-4-yl)hydrazine (2)

A solution of 5-bromo-2, 4-dichloropyrimidine (**1**) (0.01 mol) in ethanol was taken in a RB flask and cooled to 0–5 °C in an ice bath. Triethylamine (0.01 mol) was added to the cold reaction mixture and then hydrazine hydrate (0.02 mol) was added slowly at 5–10 °C. The reaction mass was allowed to stir at room temperature for 1 h. The solid thus obtained was filtered, washed with chilled water and dried to afford compound **2**. $^1$H NMR (DMSO-$d_6$, 400 MHz) δ: 8.06 (s, 1H, NH), 7.85 (s, 1H, py-H), and 4.34 (s, 2H, $NH_2$).

#### 2.2.2. Synthesis of 1-(5-bromo-2-morpholinopyrimidin-4-yl)hydrazine (3)

A solution of 1-(5-bromo-2-chloropyrimidine-4-yl)hydrazine (**2**) (0.01 mol) in ethyl acetate (50 ml) was taken and morpholine (0.021 mol) was added to it. The contents were refluxed on a water bath for 1 h. The solvent was evaporated on a steam bath, water was added into crude mass and stirred for 15 min. The solid thus obtained was filtered, washed with chilled water and dried to afford compound **3**. $^1$H NMR (DMSO-$d_6$, 400 MHz) δ: 8.06 (s, 1H, py-H), 7.85 (s, 1H, NH), 4.38 (s, 2H, $NH_2$), and 3.63–3.60 (m, 8H, $4CH_2$).

#### 2.2.3. 2-(4-Propylbenzylidene)-1-(5-bromo-2 morpholinopyrimidin-4-yl)hydrazine (4a)

The product obtained from **3** (2.74 g, 0.01 mol) and 4-propylbenzaldehyde (1.48 g, 0.01 mol). $^1$H NMR (DMSO-$d_6$, 400 MHz) δ: 10.39 (s, 1H, NH), 8.40 (s, 1H, Py-H), 8.09 (s, 1H, CH), 7.59–7.56 (d, 2H, Ar–H), 7.25–7.23 (d, 2H, Ar–H, J = 9.0 Hz), 3.66–3.64 (m, 8H, $4CH_2$), 2.58–2.48 (t, 2H, $CH_2$), 1.62–1.54 (m, 2H, $CH_2$), and 0.90 (t, 3H, $CH_3$).

#### 2.2.4. 2-(2-Fluoro-3-methoxybenzylidene)-1-(5-bromo-2-morpholinopyrimidin-4-yl) hydrazine (4b)

The product obtained from **3** (2.74 g, 0.01 mol) and 2-fluoro-3-methoxybenzaldehyde (1.54 g, 0.01 mol). $^1$H NMR (DMSO-$d_6$, 400 MHz) δ: 10.67 (s, 1H, NH), 8.69 (s, 1H, Py–H), 8.12 (s, 1H, CH), 7.48 (t, 1H, Ar–H), 7.17–7.15 (d, 2H, Ar–H, J = 9.0 Hz), 3.84 (s, 3H, $CH_3$), and 3.66–3.31 (m, 8H, $4CH_2$).

#### 2.2.5. 2-(2-Fluoro-5-methoxybenzylidene)-1-(5-bromo-2-morpholinopyrimidin-4-yl) hydrazine (4c)

The product obtained from **3** (2.74 g, 0.01 mol) and 2-fluoro-5-methoxybenzaldehyde (1.54 g, 0.01 mol). $^1$H NMR (DMSO-$d_6$, 400 MHz) δ: 10.76 (s, 1H, NH), 8.62 (s, 1H, Py–H), 8.13 (s, 1H, CH), 7.41 (d, 1H, Ar–H, J = 9.0 Hz), 7.19 (s, 1H, Ar–H), 7.00 (d, 1H, Ar–H, J = 9.0 Hz), 3.75 (s, 3H, $CH_3$), and 3.67–3.62 (m, 8H, $4CH_3$).

#### 2.2.6. 8-Bromo-5-morpholino-3-(4-propylphenyl)-[1,2,4]triazolo[4,3-c]pyrimidine (5a)

The product obtained from **4a** (4.04 g) and iodobenzene diacetate (IBD) (3.86 g). FT-IR (KBr, $cm^{-1}$) $\nu$: 2959 (C–H), 1648 (C═N), 1463 (C═C), 1376 (C–N), 1112 (C–O), and 519 (C–Br). $^1$H NMR (DMSO-$d_6$, 400 MHz) δ: 7.87 (s, 1H, Py–H), 7.73–7.71 (d, 2H, Ar–H), 7.60–7.52 (m, 2H, Ar–H), 3.25–3.02 (m, 8H, $4CH_2$), 2.68–2.58 (t, 2H, $CH_2$), 1.74–1.67 (m, 2H, $CH_2$), and 1.01–0.96 (t, 3H, $CH_3$). $^{13}$C NMR (DMSO-$d_6$, 100 MHz) δ: 150.8, 145.6, 128.2, 64.8, 50.0, 37.8, 24.5, and 13.6. MS: m/z, 401.1 ($M^+$), and 403.1 (M + 2). Anal. calcd. for $C_{18}H_{20}BrN_5O$ (in %): C, 53.74; H, 5.01; and N, 17.41. Found C-53.55, H-5.19, and N-17.56.

#### 2.2.7. 8-Bromo-3-(2-fluoro-3-methoxyphenyl)-5-morpholino-[1,2,4]triazolo[4,3 c]pyrimidine (5b)

The product obtained from **4b** (4.10 g) and iodobenzene diacetate (3.86 g). FT-IR (KBr, $cm^{-1}$) $\nu$: 2922 (C–H), 1648 (C═N), 1463 (C═C), 1376 (C–N), 1305 (C–F), 1119 (C–O), and 518 (C–Br). $^1$H NMR (DMSO-$d_6$, 400 MHz) δ: 7.90 (s, 1H, Py–H), 7.37–7.35 (m, 1H, Ar–H), 7.33 (d, 1H, Ar–H), 7.28–7.22 (m, 1H, Ar–H), 3.97 (s, 3H, $OCH_3$), and 3.34–3.00 (m, 8H, $4CH_2$). $^{13}$C NMR (DMSO-$d_6$, 100 MHz) δ: 149.2, 145.8, 128.7, 65.0, 56.1, and 48.3. MS: m/z, $M^+$ 407.0 ($M^+$), and 409.1 (M + 2). Anal. calcd. for $C_{16}H_{15}BrFN_5O_2$ (in %): C, 47.07; H, 3.70; and N, 17.16. Found C-47.23, H-3.62, and N-17.32.

#### 2.2.8. 8-Bromo-3-(2-fluoro-4,5-dimethoxy-phenyl)-5-morpholin-4-yl-[1,2,4]triazolo[4,3-c]pyrimidine (5c)

The product obtained from **4c** (4.10 g) and iodobenzene diacetate (3.86 g). FT-IR (KBr, $cm^{-1}$) $\nu$: 2926 (C–H), 1638 (C═N), 1462 (C═C), 1376 (C–N), 1304 (C–F), 1112 (C–O), and 515 (C–Br). $^1$H NMR (DMSO-$d_6$, 400 MHz) δ: 7.90 (s, 1H, Py–H), 7.30 (s, 1H, Ar–H), 7.18 (s, 1H, Ar–H), 3.95 (s, 3H, $OCH_3$) 3.87 (s, 3H, $OCH_3$), and 3.37–3.05 (m, 8H, $4CH_2$). $^{13}$C NMR (DMSO-$d_6$, 100 MHz) δ: 152.2, 138.6, 124.7, 65.7, 56.1, and 49.3. MS: m/z, $M^+$ 437.0 ($M^+$), and 439.1 (M + 2). Anal. calcd. for $C_{16}H_{15}BrFN_5O_2$ (in %): C, 47.07; H, 3.70; and N, 17.16. Found C-47.15, H-3.66, and N-17.26.

Synthesized molecules (**5a–c**) were structurally characterized by mass, $^{13}$C NMR, $^1$H NMR and FT-IR spectral studies. 8-Bromo-5-morpholino-3-aryl-1,2,4-triazolo[4,3-f] pyrimidines (**5a–c**) were prepared by the method summarized in Scheme 1. The chemical structures and physical data of all the synthesized compounds are tabulated in Table 1. The spectral data (IR $^1$H NMR, and mass) of all the synthesized compounds were in full agreement with the proposed structures.

### 2.3. Weight loss measurements

Using an analytic balance (precision: ±0.1 mg), the specimen initial weight was recorded before immersion. MS specimens were immersed in the acid solutions for 6 h at different temperatures. The temperature of the environment was maintained by thermostatically controlled water bath with accuracy of ±0.2 °C (Weiber limited, Chennai, India), under aerated condition. After 6 h of immersion, the specimens were removed, rinsed in water and acetone and dried in desiccator. The weight loss was recorded to the nearest 0.0001 g using analytical balance (Sartorius, precision ±0.1 mg). The average weight loss of