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## Synthesis Some New Heterocyclic Compounds By Domino Reactions, and Study Them as Corrosion Inhibitors.

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### ABSTRACT

*One-pot* synthesis of 5-(4-methylpiperazin-1-yl)-1,3,5-dithiazinane via domino reactions of 1- amino - 4- methylpiperazine with formaldehyde, and hydrogen sulfide was carried out. Multicomponent reaction of 2- methylpiperazine with formaldehyde and hydrogen sulfide passes on the way of intermolecular heterocyclisation to form 6,13-dimethyl-3,10-dithia- 1,5,8,12-tetraazatricyclo [10.2.2.2<sup>5,8</sup>]octadecane. This reaction takes place by way of intramolecular heteroring with the selective formation of 6-methyl-3-thia-1,5-diazabicyclo [3.2.2]nonane ,under same conditions, but strong dilution for about (4 times) at 0 ° C. It is shown that synthetic binuclear sulfur- and nitrogen-containing heterocycles provide effective protection to carbon steel from acid corrosion, where reached the inhibition efficiency to 88.15%, and 96.6%, whereas the tricycle hetero compound was less 83.7 %.

**Keywords:** Heterocyclic compounds, inhibitors, EDX, AFM, Carbon steel corrosion.

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## INTRODUCTION

For the protection of oilfield equipment by using inhibitors based on quaternary ammonium salts is one of the most appropriate methods of corrosion control [1,2]. Nitrogen heterocyclic compounds and their complex are characterized with high protective properties due to their effective adsorption capacity [3]. Large numbers of organic compounds are revealed that contain nitrogen, sulfur, and oxygen are good corrosion inhibitors [4]. Nitrogen-based organic inhibitors, such as imidazolines or their salts have been successfully used in these applications even without an understanding of the inhibition mechanism. Most organic compounds are facilitated adsorption by the presence of polar groups in the molecular structure which can strongly adsorb onto the metal surface or react with the corrosion product on the surface to form a protective layer [5]. Heterocyclic compounds through owning hetero atoms such as nitrogen, sulfur, and oxygen, and also because of their multiple bonds in their structure facilitate the molecule's adsorption on the metallic surfaces Fe, Zn, Al, Mg [6-9]. The injection of organic compounds as a corrosion inhibitor is the usual practice in oil, and gas production systems to control internal corrosion of carbon steel structures [10-12].

The aim of this study is to find effective inhibitors for inhibiting corrosion metal in acidic media. Heterocyclic compounds which containing N, and S formation a protective film on metal surfaces as a result of adsorption and chemisorptions, and these process are occur tandem. N-quaternary cations are very promising as inhibitors of acid corrosion of anionic and cationic types. Furthermore, sulfur can form covalent bonds with metals, together with complex linkages.

The basis of the synthesis, we used a multicomponent thiomethylation reaction of amines with formaldehyde, and hydrogen sulfide (H<sub>2</sub>S), which leads to the formation, as it is known 1,3,5-dithiazinanes [13,14].

Substituted piperazine that containing several amino groups per molecule were involved in thiolmethylation reaction in order to assembly binuclear heterocyclics. Also should be added H<sub>2</sub>S in the synthesis of heterocyclics is a profitable strategy from the standpoint of "Green Chemistry", as hydrogen sulfide is a man-made product resulting from a huge scale during hydrotreated sour crude oil.

## EXPERIMENTAL

### Instruments

<sup>1</sup>H and <sup>13</sup>C NMR spectrum where recorded on a Bruker AM 500 spectrometer, and CDCl<sub>3</sub> was used as solvent. Also used GC- mass spectra of compounds **3-5**, **A-C** were obtained with electron ionization (70 eV) on a GCMS-QP2010 Ultra (Shimadzu) gas chromatography-mass spectrometer (Supelco 5ms capillary column 60000×0.25; carrier gas helium; oven temperature programming from 40 °C to 150 °C at a rate of 10 deg/min; injector temperature 260°C; ion source temperature 200°C). Infrared spectra were recorded on FTIR-8400 spectrometer (Shimadzu) in the (600-4000) cm<sup>-1</sup>. While Energy dispersive X-ray Fluorescence Spectrometer (EDX) used to obtain activity of these compounds as corrosion inhibitor by using Energy dispersive X-ray fluorescence spectrometer EDX-800HS (Shimadzu). The EDX tests were performed at Voltage 15 – 50 kv., current 20 – 100 mv., each experiment in the instrument needs to be from 10 to 15 minutes, and the measurements were carried out under vacuum pressure.

Atomic Force Micrograph (AFM). The surface morphology of carbon steel plates was investigated by using atomic force microscope (AFM). Atomic force microscopy was performed using Agilent 5500 AFM, USA. Imaging for this study was conducted in AC mode with PPP-NCL probes (Nanosensor, Switzerland). The resonance frequency and force constant of cantilever are 185 kHz, and 43 N/m, respectively. The samples were cleaned with distilled water, dried, and then used for AFM. The commercial software Pico Image Basic ver. 5.1 from Agilent Technologies was used for determination of roughness parameters.

## Synthesis of heterocyclic compounds 3 - 5

### Synthesis compound 3 (A) : 5-(4-Methylpiperazin-1-yl)-1,3,5-dithiazinane

In three - neck flask, were placed aqueous 10 % formaldehyde (150 mmol), 30 ml absolute ethanol, and added bubbled hydrogen sulfide (100 mmol) with stirring for 1 hour at temperature 0 °C, then added 1-amino-4-methyl piperazin (50 mmol) as a dropwise to the mixture. After that the product extracted from the mixture with chloroform, and dried with Na<sub>2</sub>SO<sub>4</sub>. From GC-Mass spectrum it was observed that the percentage of compound was few (19.6%), which led to change the sequence of steps the previous procedure. Therefore, ( procedure 2) aqueous 10 % formaldehyde (150 mmol) were stirred with 1- amino-4-methyl piperazin (50 mmol), and 30 ml absolute ethanol for 2 hour at temperature 0 °C, after that the reaction was allowed to reach to room temperature, then added bubbled hydrogen sulfide (100 mmol) for 1 hour, and also the product was extracted from the mixture with chloroform, and dried with Na<sub>2</sub>SO<sub>4</sub> for about 5 hours, then evaporated. The yield was 77%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 1.42 (s, 3H, CH<sub>3</sub>-N); 2.2- 2.7 (t, 4H, CH<sub>3</sub>-N-CH<sub>2</sub>); 3.1- 3.26 (t, 4H, CH<sub>2</sub>-CH<sub>2</sub>-N); 3.77 (br, s, 2H, S-CH<sub>2</sub>-S); 4.22 (s, 4H, N-CH<sub>2</sub>-S). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ = 35.8 (CH<sub>3</sub>); 50.57 (2C, CH<sub>3</sub>-N-CH<sub>2</sub>); 57.80 (2C, CH<sub>2</sub>-CH<sub>2</sub>-N); 59.83 (2C, N-CH<sub>2</sub>-S); 40.33 (1C, S-CH<sub>2</sub>-S). MS, m/z (I<sub>rel</sub> (%)) : 219 [M]<sup>+</sup> (8.3); 100 [C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>]<sup>+</sup> (100); 98 [C<sub>5</sub>H<sub>10</sub>N<sub>2</sub>]<sup>+</sup> (29.8); 70 [C<sub>4</sub>H<sub>8</sub>N]<sup>+</sup> (18.7); 56 [C<sub>2</sub>H<sub>4</sub>N<sub>2</sub>]<sup>+</sup> (39.3); 42 [C<sub>2</sub>H<sub>4</sub>N]<sup>+</sup> (19.8). IR (cm<sup>-1</sup>) 1240.77 C-N; 1060.88 N-N, 640.10 C-S; 2990.71 and 2940.37 C-H stretching. Elemental Analyses calculated For C<sub>8</sub>H<sub>17</sub>N<sub>3</sub>S<sub>2</sub>: C 43.83; H 7.76; N 19.17; S 29.22; Found C 43.67; H 7.49; N 19.34; S 29.44.

### Synthesis 4 (B): 6,13-Dimethyl-3,10-dithia-1,5,8,12-tetraaza-tricyclo[10.2.2.2<sup>5,8</sup>] octadecane.

A mixture consist of formaldehyde solution (10 %) (100 mmol), 25 ml absolute ethanol and 2-methyl piperazin (50 mmol) were stirred for 2 hour at temperature 0 °C, then added bubbled hydrogen sulfide (100 mmol) for 1 hour at room temperature, to produce white precipitate which was collected. Yield was 80%. It's m.p. was 123-125°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 1.0 -1.18 (d, 6H, CH<sub>3</sub>-CH); 2.5-2.77 (m, 2H, CH<sub>3</sub>-CH-CH<sub>2</sub>); 3.0 - 3.15 (d, 4H, N-CH<sub>2</sub>-CH); 3.25-3.4 (t, 8H, N-CH<sub>2</sub>-CH<sub>2</sub>); 3.66 (s, 8H, N-CH<sub>2</sub>-S). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ = 16.82 (2C, CH<sub>3</sub>); 61.61 (2C, CH<sub>3</sub>-CH-CH<sub>2</sub>); 50.32 (2C, N-CH<sub>2</sub>-CH); 55.66 (4C, N-CH<sub>2</sub>-CH<sub>2</sub>-N); 40.32 (4C, N-CH<sub>2</sub>-S). MS, m/z (I<sub>rel</sub> (%)) : 316[M]<sup>+</sup> (50); 286[M-C<sub>2</sub>H<sub>6</sub>]<sup>+</sup> (75); 100[C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>]<sup>+</sup> (86); 60[C<sub>2</sub>H<sub>4</sub>S]<sup>+</sup> (33); 192[C<sub>7</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>]<sup>+</sup> (53); 70[C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>]<sup>+</sup> (20); 56[C<sub>2</sub>H<sub>4</sub>N<sub>2</sub>]<sup>+</sup> (27); 158[C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>S]<sup>+</sup> (100). IR (cm<sup>-1</sup>) 1342.44 C-N; 720.37 C-S; 2940.27 and 2880.15 C-H stretching. Elemental Analyses calcd. For C<sub>14</sub>H<sub>28</sub>N<sub>4</sub>S<sub>2</sub>: C 53.16; H 8.86; N 17.72; S 20.25; Found C 52.83; H 9.02; N 17.30; S 20.47.

### Synthesis compound 5 (C): 6-Methyl-3-thia-1,5-diaza-bicyclo [3.2.2] nonane.

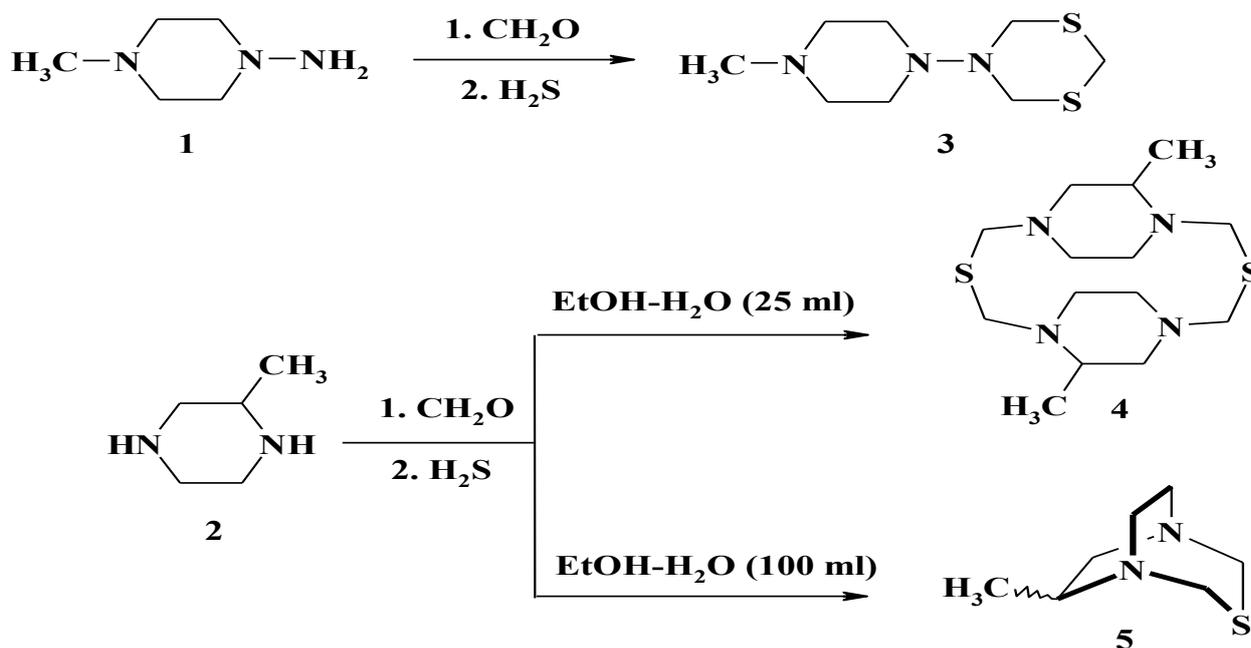
The mixture of aqueous 10 % formaldehyde (100 mmol), 100 ml absolute ethanol, and 2-methyl piperazine (50 mmol) was stirred for 2 hour at temperature 0 °C, then added bubbled hydrogen sulfide (100 mmol prepared from calculated amounts of Na<sub>2</sub>S and HCl) for one hour. After that, ethanol was evaporated, then the product were extracted from the mixture with chloroform. Extract was dried by Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The yield was (79 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 0.90-1.04 and 1.08-1.25 (d, 3H, a and e CH<sub>3</sub>-CH, <sup>3</sup>J = 33.9 Hz and <sup>3</sup>J = 25.9 Hz); 2.60 (br. s, 4H, N-CH<sub>2</sub>-S); 4.2-4.5 (d, 2H, N-CH<sub>2</sub>-CH); 3.65-4.15 (m, 1H, CH<sub>3</sub>-CH-CH<sub>2</sub>); 3.27-3.51 (H<sub>a</sub>) and 4.70-4.92 (H<sub>b</sub>) (d, 4H, N-CH<sub>2</sub>-CH<sub>2</sub>-N, <sup>2</sup>J = 32.2 Hz). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, δ): 13.9 and 16.5 (a and e CH<sub>3</sub>); 50.88 (1C, N-CH<sub>2</sub>-CH-); 52.0 (1C, CH<sub>3</sub>-CH-CH<sub>2</sub>); 58.2 (2C, N-CH<sub>2</sub>-S); 63.7 (2C, N-CH<sub>2</sub>-CH<sub>2</sub>-N). MS, m/z (I<sub>rel</sub> (%)) : 158 [M]<sup>+</sup> (100); 143 [M- CH<sub>3</sub>]<sup>+</sup> (17); 84 [C<sub>5</sub>H<sub>10</sub>N]<sup>+</sup> (93); 70 [C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>]<sup>+</sup> (30); 56 [C<sub>2</sub>H<sub>4</sub>N<sub>2</sub>]<sup>+</sup> (27); 42 [C<sub>2</sub>H<sub>4</sub>N]<sup>+</sup> (37); and mass to second isomer is 158 [M]<sup>+</sup> (73.3); 125 [C<sub>5</sub>H<sub>5</sub>N<sub>2</sub>S]<sup>+</sup> (100); 70 [C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>]<sup>+</sup> (68.7); 84 [C<sub>5</sub>H<sub>10</sub>N]<sup>+</sup> (36.7); 143 [M- CH<sub>3</sub>]<sup>+</sup> (3.8); 56 [C<sub>2</sub>H<sub>4</sub>N<sub>2</sub>]<sup>+</sup> (77.4); 42 [C<sub>2</sub>H<sub>4</sub>N]<sup>+</sup> (40.1); 111 [C<sub>6</sub>H<sub>11</sub>N<sub>2</sub>]<sup>+</sup> (20.0); 102 [C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>S]<sup>+</sup> (18.9); IR (cm<sup>-1</sup>) 1193.15 C-N; 620.86 C-S; 2970.77 and 2945.55 C-H stretching. Elemental Analyses calculated For C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>S: C 53.16; H 8.86; N 17.72; S 20.25; Found C 52.88; H 8.54; N 17.75; S 20.63.

## RESULTS AND DISCUSSION

### Multicomponent thiomethylation of piperazines.

The raw materials are used heterocyclic amines 1-amino-4-methylpiperazine (**1**), and 2-methylpiperazine (**2**). The reaction that known thiolmethylation [15] was used the compounds (**1**), and (**2**) with mixture of CH<sub>2</sub>O – H<sub>2</sub>S (3:2), where is passed bubbling H<sub>2</sub>S in formalin (10%), even behave raw materials be

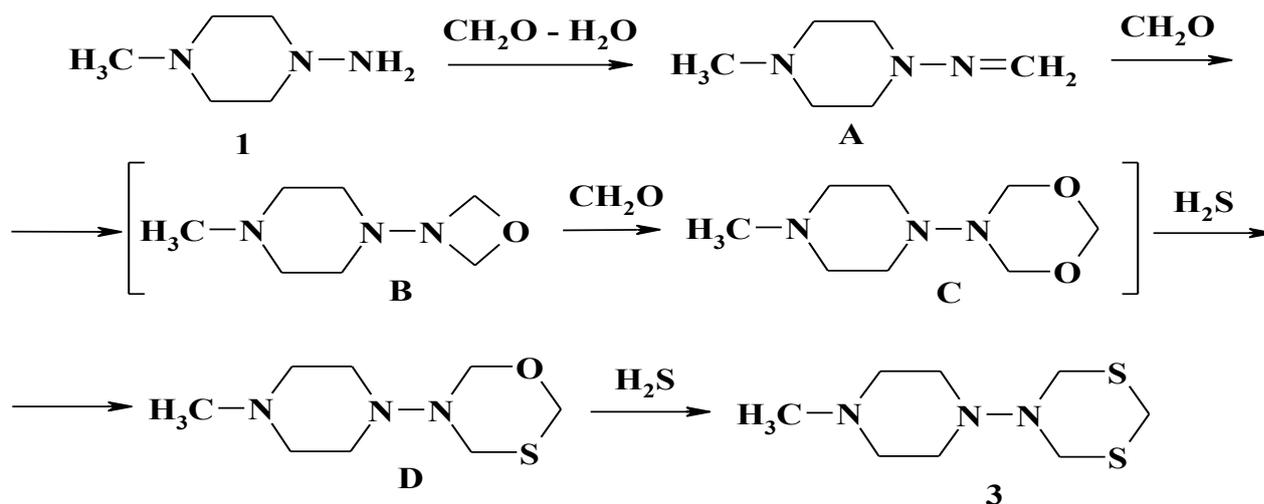
non-selective. According to thiolmethylation reaction the compound 1-amino-4-methylpiperazine (**1**) has given the target compound 5-(4-Methylpiperazin-1-yl)-1,3,5-dithiazinane (**3**), through selectivity of the synthesis that depends on the temperature, sequences addition of the reactants, and their concentrations. The result of reaction 1-amino-4-methylpiperazine (**1**) in ethanol solution with the aqueous solution of formaldehyde (10%) at a molar ratio 1: 3 (scheme 1) and 0° C followed by bubbling an excess amount of H<sub>2</sub>S (~ 3 mol) in the reaction mixture, so the product (**3**) from this reaction has a yield of 77% . Using this methodology thiolmethylation with 2-methylpiperazine (**2**), which having two secondary amino groups, resulting in the formation 6,13- dimethyl-3,10-dithia-1,5,8,12-tetraazatricyclo[10.2.2.2<sup>5,8</sup>] octadecane (**4**), this product is intermolecular heterocyclic that consist from two molecules of the compound (**2**), four molecules of CH<sub>2</sub>O and two molecules of H<sub>2</sub>S. In order to the implementation of the intramolecular heterocyclization with compound (**2**) was used a strong dilution (4 times) to reaction mixture. In these conditions occur selectively forming 6-methyl-3-thia-1,5- diazabicyclo [3.2.2] nonane (**5**) (scheme 1).



The structures of the compounds 3 - 5 was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR, IR, GC-mass spectrometry, and elemental analyses CHNS. The mass spectra for all the compounds observed peaks of molecular ions. Note that for the bicycle (**5**) recorded two compounds (C) with a molecular ion [M] m / z 180. probably due to the spatial isomerism of the methyl group formed *a* and *e* isomers. Indeed, <sup>1</sup>H NMR and <sup>13</sup>C are shown on two signals in δ 0.9-1.04 , and 1.08-1.25 ppm protons of the methyl groups and in δ 13.9 and 16.5 ppm methyl group carbon atoms. <sup>1</sup>H NMR spectrum also observed bridging ethylene protons as doublets at 3.27-3.51, and 4.70-4.92 ppm.

#### Proposed mechanism of multicomponent thiomethylation of 1-amino-4-methylpiperazine.

It should be noted that multicomponent reaction thiolmethylation is a domino process that consist of several steps, where monitoring the progress of the reaction was carried by GC-MS. Determination of the composition intermediate products were performed by sampling the reaction mixture during two hours. Found that initially amine **1** with CH<sub>2</sub>O forms imine **A** (m / z 127.156), which is further undergoes to cyclocondensation with CH<sub>2</sub>O at first to **B** (m / z 157.100), and then to **C** (m / z 187.103), (scheme 2) . This process is carried out at 0 ° C for about 2 hours. After that added H<sub>2</sub>S bubbling into the reaction mixture leads to a successive replacement of the oxygen atoms in C to sulfur atoms by Yuriev reaction [16] to obtain **D** (m / z 203.107), and then the target **3** (m / z 219.107). It should be emphasized, that a complete conversion intermediate C and D to product 3 requires continuous bubbling H<sub>2</sub>S. In this regard, in the reaction using an excess amount of H<sub>2</sub>S (~ 3 mol).



We note that when bubbling  $H_2S$  in the reaction mixture in small quantities recorded D (m / z 203.107). Thus, when one-pot thiomethylation amino substrates 1 and 2 with  $CH_2O$  and excess  $H_2S$  to replace all oxygen atoms to sulfur.

**Anticorrosion studies of 5-(4-methylpiperazin-1-yl)-1,3,5-dithiazinane (A), 6,13-dimethyl-3,10-dithia-1,5,8,12-tetraazatricyclo [10.2.2.2<sup>5,8</sup>] octadecane (B), and 6-methyl-3-thia-1,5-diazabicyclo[3.2.2]nonane (C)**

#### Energy dispersive X-ray Fluorescence Spectroscopy.

The prepared heterocycles compounds (3-5) containing hetero rings N, and S are promising corrosion inhibitors due to their ability to form both Van der Waals or covalent bonds on the metal surface. Properties of the above compounds as a corrosion inhibitor were studied, and carbon steel alloy type N-80 used in this study, its composition of 98.227% iron as shown in the (Table 1).

**Table 1: Represent of components of alloy**

Elements	Fe (%)	C (%)	Mn (%)	Si (%)	Cu (%)	Cr (%)	S (%)
Percentage %	98.227	0.2	0.841	0.366	0.190	0.152	0.024

Anticorrosive properties are investigated according to the standard procedure<sup>[17]</sup> at 25°C after immersed (5hrs) in 0.5 M HCl, and once again with presence of inhibitors based compounds 3 - 5 by fluorescence spectroscopy.

The corrosion in acidic solutions, as is known, the destruction of metal alloys is due to the oxidation of iron to iron oxide, and as a consequence there is an increase in oxygen mass at without inhibitors as shown (Table 2). Assessment of the weight loss ( $\theta$ ) of element (%) in the alloy was calculated using the formula,  $\theta = \frac{W_0 - W_i}{W_0} \cdot 100$ , where ( $W_0$ ) element content in the fresh carbon steel alloy, and ( $W_i$ ) element content in the corroded alloy. Inhibition efficiency (%) was determined according to the formula  $IE = \frac{\theta_0 - \theta_i}{\theta_0} \cdot 100$ , where ( $\theta_0$ ), ( $\theta_i$ ) weight loss of element (%) absences, and presences inhibitors respectively. The results are shown in tables 2 and 3.

**Table 2: The percentages of all elements in the alloy after corrosion determined by X-ray- fluorescence spectroscopy**

Sample	Element (%) Fe	Element (%) O	Element (%) C	Element (%) Mn	Element (%) Si	Element (%)Cu	Element (%) Cr	Element (%) S	Element (%) Cl
Fresh Carbon Steel	98.227	-----	0.2	0.841	0.366	0.190	0.152	0.024	-----
Carbon Steel without inhibitors	78.359	19.031	0.39	0.670	0.203	0.132	0.133	0.022	1.06
Carbon Steel with inhibitor 3 (A)	95.853	0.195	0.45	0.751	0.333	0.181	0.141	2.096	-----
Carbon Steel with inhibitor 4 (B)	94.958	2.384	0.34	0.731	0.354	0.180	0.151	0.675	0.227
Carbon Steel with inhibitor 5 (C)	97.542	0.136	0.41	0.720	0.321	0.162	0.143	0.566	-----

**Table 3: The percentages of corroded iron, and inhibition efficiency of compounds 3 – 5**

Compounds	Weight loss of iron (%) ( $\theta$ )	Inhibition efficiency (%)
Without inhibitor	20.0	-----
Inhibitor 3(A)	2.37	88.15
Inhibitor 4(B)	3.26	83.70
Inhibitor 5(C)	0.68	96.60

It is clear from the results, weight loss(%) from Fe without inhibitor 20% , while adding the compounds **3 - 5** as a inhibitors at concentration 0.005 M, it can be observed mass loss of iron as follows 2.37% with inhibitor **3**, 3.26% with inhibitor **4**, and 0.68% with inhibitor **5**, (Table3). Furthermore, percentages of sulfur in carbon steel alloy with inhibitors , is higher than percentages of sulfur in fresh carbon steel (Table.2). This is due to the fact that sulfur enters in the contents of inhibitors that used, and that indicate that the inhibitors molecules adsorbed on the metal surface [18]. Finally, the degree of effectiveness of inhibiting increased in the order  $4 < 3 < 5$  , and which reached to 83.7%, 88.15%, 96.6%, respectively (Table.3).

**Atomic Force Micrograph (AFM).**

In order to establish whether inhibition is due to the formation of a film on the metal surface through adsorption, atomic force micrographs were studied [19]. Surface roughness analysis for carbon steel immersed (5hrs) in the 0.5M HCl at 25°C, and presence the compounds (**3 -5**) , and surface roughness analysis for polished carbon steel metal surface (reference) was studied by using atomic force microscopy.

Table 4 shows the parameters obtained when using the AFM technique, such as the values of Sa, Sp, Sv, and Sz for the polished carbon steel alloy surface (reference) are( 26, 98, 102, and 200) nm, which show more homogeneous surface compared with blank (256, 1470, 995 and 2465) nm respectively, this indicate that blank has a greater surface roughness than the polished metal surface. Furthermore, this shows that the unprotected carbon steel alloy surface is rougher due to the corrosion of metal in aqueous solution of hydrochloric acid [20,21] ( Figure 1: G and H).

It is clear from the parameters of AFM (Table 4) when the presence 0.005 M of compound **A (3)** in aqueous solution of hydrochloric acid leads to decrease the average roughness (Sa) value from 256 nm in blank to 39.9 nm with inhibitor. The large difference in these parameters confirms that the surface appears smoother (Figure 1: E), due to the formation of a compact protective film [22,23].

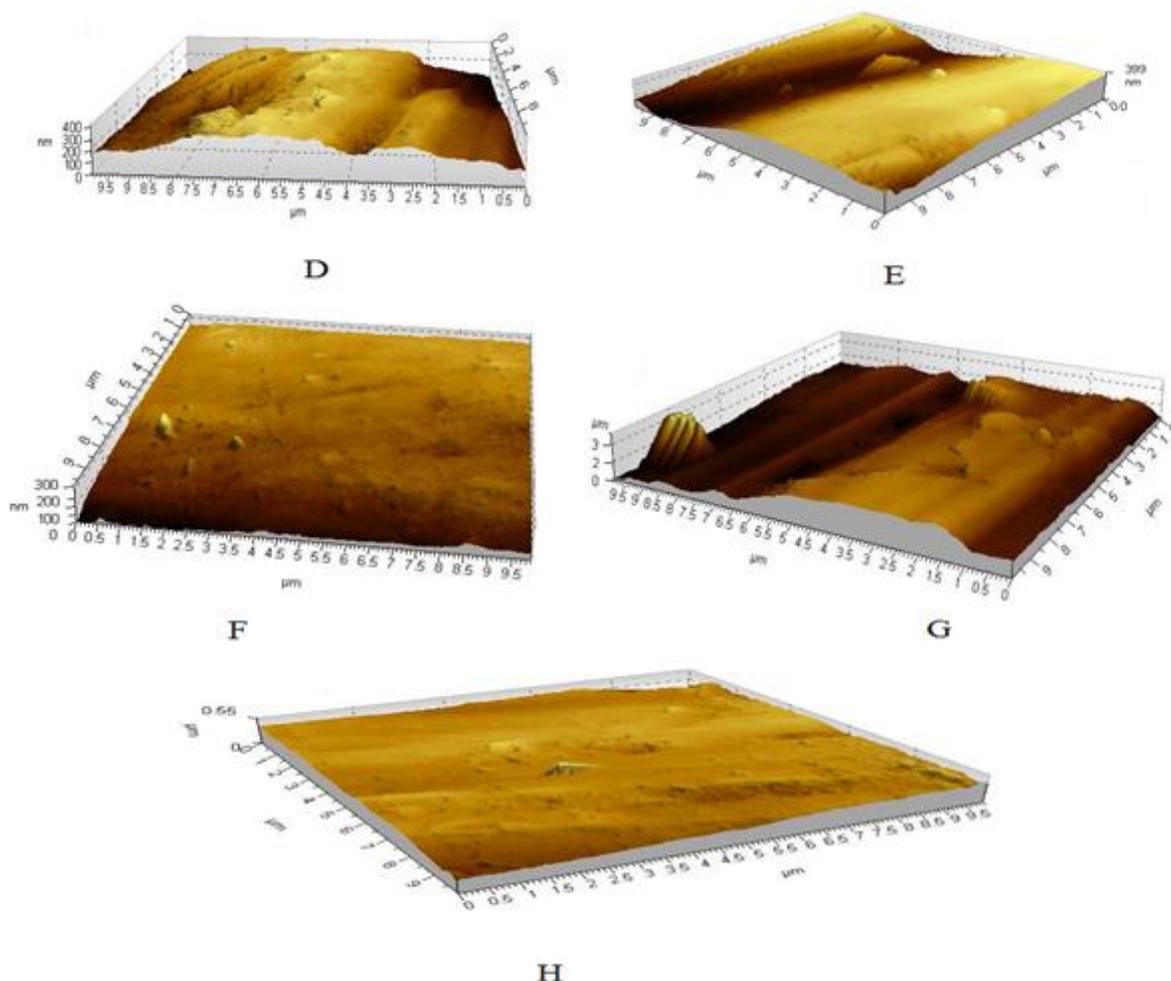
Regarding to , compound **B (4)** leads to decreased the Sa,Sp,Sv, and Sz values from (256, 1470, 995,2465), nm in blank to ( 57.2, , 258, 136, 394) nm with inhibitor respectively ( Figure 1: D). 3D AFM images, displays the corroded carbon steel surface with few valleys [5,24] .

As well as, presence compound **C (5)** as a corrosion inhibitor shows high efficiency. The 3D AFM image of the surface carbon steel are similar in a large extent with 3D AFM images of the polished surface carbon steel. Regarding to the average roughness value is significantly reduced to 30 nm when compared with 256 nm of blank, and slightly increased to 30 when compared with the polished carbon steel surface( reference). The Sz, Sp, and Sv values have decreased from (2465, 1470, 995) nm in aqueous solution of hydrochloric acid(blank) to(282, 115, 167) nm with inhibitor respectively. This shows that the surface is more homogenous, and confirms the formation of the film on the metal [21,25] ( Figure 1: F).

**Table 4 : Roughness parameters of arithmetic mean deviation of the surface of carbon steel from Atomic force micrograph**

Sample	Value(nm)			
	Sp	Sv	Sa	Sz
Polished carbon steel	98	102	26	200
Carbon Steel without inhibitor(Blank)	1470	995	256	2465
Carbon Steel with inhibitor <b>3(A)</b>	154	188	39.9	342
Carbon Steel with inhibitor <b>4(B)</b>	258	136	57.2	394
Carbon Steel with inhibitor <b>5(C)</b>	115	167	30.0	282

Finally, it can be concluded that saturated N- and S-heterocycles by physical and chemical sorption to form the protective layer reducing the roughness on the carbon steel surface. Compound **C (5)** is a leader among the synthesized compounds that are experienced by us as inhibitors of acid corrosion, which is confirmed by AFM, and energy dispersive X-ray- fluorescence spectroscopy.



**Figure 1.** AFM Images of carbon steel without inhibitor (0.5M HCl),(G) ,and polished carbon steel (H). Carbone steel with inhibitor 3(0.5 M HCl + 0.005 M 3), (E). Carbone steel with inhibitor 4 (0.5 M HCl + 0.005 M 4), (D). Carbone steel with inhibitor 5 (0.5 M HCl + 0.005 M 5), (F)

The surface roughness of AFM samples can be quantified according to average roughness ( $S_a$ ), maximum depth of valleys ( $S_v$ ) and maximum height of summits ( $S_p$ ) normalized in the ISO 4287 standard (Table 4).

$$S_a = \frac{1}{NM} \sum_{x=0}^{N-1} \sum_{y=0}^{M-1} |z_{x,y}|$$

$S_a$  – Arithmetic mean deviation of the surface

$S_p$  - Height between the highest peak and the mean plane.

$S_v$  - Depth between the mean plane and the deepest valley

### CONCLUSION

A one-pot, four-step domino thiomethylation process has been developed for the direct synthesis of bi- and tri nuclear heterocyclics starting from  $H_2S$ ,  $CH_2O$ , and substituted piperazines. As a result, for the first time, the synthesis of novel 5-(4-methylpiperazin-1-yl)-1,3,5-dithiazinane, 6-methyl-3-thia-1,5-diazabicyclo [3.2.2] nonane, and 6,13-dimethyl-3,10-dithia-1,5,8,12-tetraazatricyclo [10.2.2.2<sup>5,8</sup>] octadecane was carried out. It has been established that inhibition of acidic corrosion using *N*-, *S*-heterocycles is due to the formation of monolayer film on the steel surface. All prepared heterocyclic compounds were inhibited corrosion process that occurs on C-steel in 0.5 M HCl, and compound C, which contain two isomers, can be concluded that it is the best prepared compounds to inhibition corrosion in 0.5 M HCl.

### REFERENCES

- [1] C.M. Reshetnikov: (1986), Inhibitors acid corrosion of metals, J. Chemistry, 4: 144 - 152.
- [2] E.C. Ivanov: (1986), The inhibitors of metal corrosion in acidic environments, Published by Metallurgy Moscow, Russia, 175.
- [3] Patent 2402641 PΦ. Acid corrosion inhibitors and methods for their preparation // Alykov N.M., Velikorodov A.V., Pichugin E.A.// Published 27.10.2010.
- [4] A.Y. El - Etre and M. Abdallah: (2000), Natural honey as corrosion inhibitor for metals and alloys. II. C-steel in high saline water, J. Corrosion Science, 42: 731-738.
- [5] R. M. Alagta: (2009), M.Sc Thesis, Investigation of Carbon Steel Corrosion Inhibition by Hydroxamic Acids , Budapest university of technology , department of chemical and environmental process engineering.
- [6] M .S. El-Sayed, A. M. El Shamy, M .R. Mostafa and A.O.H. El Nazhawyb: (2007), 5-(Phenyl)-4H-1,2,4-triazole-3-thiol as a corrosion inhibitor for copper in 3.5% NaCl solutions, J. Materials Chemistry and Physics, 102: 231-239.
- [7] K. F Khaleda, S. A. Fadel-Allahb and B. Hammoutic: (2009), Some benzotriazole derivatives as corrosion inhibitors for copper in acidic medium, J. Materials Chemistry and Physics, 117:148–155.
- [8] G. Avci : (2008), Inhibitor effect of N,N-methylene diacrylamide on corrosion behavior of mild steel in 0.5M HCl, J. Materials Chemistry and Physics, 112: 234–238.
- [9] S. K Shukla and M. A Quraishi: (2010), A new and efficient corrosion inhibitor for mild steel in hydrochloric acid solution, J. Materials Chemistry and Physics, 120: 142–147.
- [10] F. Farelas and A. Ramirez: (2010), Carbon Dioxide Corrosion Inhibition of Carbon Steels Through Bis-imidazoline and Imidazoline Compounds Studied by EIS, J. Electrochemical Science, 5: 797-814.
- [11] L. Feng, H. Yang and F. Wang: (2012), Effect of an Imidazoline Derivative on the Protection Performance of Oxide Film Formed on Carbon Steel in Saturated  $Ca(OH)_2$  Solution, J. Electrochemical Science, 7: 4064-4077.
- [12] S. Chen, S. Scheiner, T. Kar and U. Adhikari: (2012), Theoretical Study on Relationship Between Structure of Mercapto-Triazole Derivatives and Inhibition Performance, J. Electrochemical Science, 7: 7128 -7139.
- [13] V.R. Akhmetova, G.R. Nadyrgulova, Z.T. Niatshina and U.M. Dzhemilev: (2009), Cyclothiomethylation of primary amines with formaldehyde and hydrogen sulfide to nitrogen- and sulfur-containing heterocycles (review) , J. Chemistry of Heterocyclic Compounds, 45: 1155-1176.
- [14] [V.R. Akhmetova](#), [G.R. Khabibullina](#), E.B. [Rakhimova](#), [R.A. Vagapov](#), [R.R. Khairullina](#), Z.T. [Niatshina](#) and N.N. [Murzakova](#): (2010), Multicomponent reactions of amines with aldehydes and  $H_2S$  as efficient rout to heterocyclics and thioaza macrocycles , J. Mol Divers, 14: 463-471.

- [15] V.R. Akhmetova, G.R. Nadyrgulova, Z.T. Niatshina, R.R. Khairuiina, Z.A. Starikova, A.O. Borisova, M. Yu. Antipin, R.V. Kunakova, and U.M. Dzhemilev: (2009), Cyclothiomethylation of functional substituted anilines by CH<sub>2</sub>O and H<sub>2</sub>S, *J. Heterocycles*, 78: 45-57.
- [16] Vatsuro K.V. and Mishchenko G. L.: (1976), *Named Reactions in Organic Chemistry*, Published by Moscow chemistry, Russia, 538.
- [17] A.K. Singh and M.A. Guraishi: (2012), Study of some bidentate Schiff bases of isatin as corrosion inhibitors for mild steel in hydrochloric acidic solution, *J. Electrochemical Science*, 7: 3222-3241.
- [18] A.S. Fouda, G.Y. Elewady, K. Shalabi and S. Habbouba: (2014), Gibberellic acid as green corrosion inhibitor for carbon steel in hydrochloric acid solutions, *J. Materials and Environmental Science*, 5 : 767-778.
- [20] S. John and A. Joseph: (2012), Electro analytical, surface morphological and theoretical studies on the corrosion inhibition behavior of different 1,2,4-triazole precursors on mild steel in 1 M hydrochloric acid, *J. Materials Chemistry and Physics*, 133: 1083-1091.
- [21] M. Mobin and S. Masroor: (2012), Cationic Gemini Surfactants as Novel Corrosion Inhibitor for Mild Steel in 1M HCl, *J. Electrochemical science*, 7: 6920-6940.
- [22] R.H. Zadeh, I. Danaee and M.H. Maddahy: (2013), Thermodynamic and Adsorption Behaviour of Medicinal Nitramine as a Corrosion Inhibitor for AISI Steel Alloy in HCl Solution, *J. Materials Science Technology*, 29: 884-892.
- [23] S. Gowria, J. Sathiyabama, S. Rajendran, Z. Robert Kennedy and S. Agiladevi: (2013), Corrosion Inhibition of Carbon Steel in Sea Water by Glutamic Acid - Zn<sup>2+</sup> System, *J. Chemical Science Transactions*, 2: 275-281.
- [24] M. Dahmani, A. Et-Touhami, S.S. Al-Deyab, B. Hammouti and A. Bouyanzer: (2010), Corrosion Inhibition of C38 Steel in 1 M HCl: A Comparative Study of Black Pepper Extract and Its Isolated Piperin, *J. Electrochemical Science*, 5: 1060-1069.
- [25] M. Hakeem, S. Rajendran and A.P. P. Regis: (2014), Calcium Gluconate As A Corrosion Inhibitor For Aluminium, *J. Engineering, Computers and Applied Sciences*, 3: 1-11.
- [26] P. P. Raymond, A.P. P. Regis, S. Rajendran and M. Manivannan: (2013), Investigation of Corrosion Inhibition of Stainless steel by Sodium tungstate, *J. Chemical Sciences*, 3: 54-58.