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Sayed AS Mousa
Department of Chemistry, Faculty of Science, Al-Azhar University, Assiut, Egypt

Correspondence
Sayed AS Mousa
Department of Chemistry, Faculty of Science, Al-Azhar University, Assiut, Egypt

Synthesis, characterization and corrosion inhibition of Pyrazolo[1,5-a][1,8]naphthyridine, Pyrazolo[1,5-a]pyridine and Pyrazolo[1,5-a]pyrimidine derivatives, quantum chemical approach

Sayed AS Mousa

Abstract
The behavior of 3-amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile 1 towards some electrophiles such as arylidens, enamines is reported to afford pyrazolo[1,5-a][1,8]naphthyridine derivative 4, pyrazolo[1,5-a]pyridine derivatives 8, 10 and pyrazolo[1,5-a]pyrimidine derivatives 12a,b and 14. Also, reaction of pyrazole 1 with DMFDMA afforded enamine 16 which reacts with hydrazine hydrate and malononitrile to give tricyclic compound 17 and pyrazolo[1,5-a]pyrimidine derivative 18 respectively. The inhibition effect of tested compounds at 1.0 M H_2SO_4 was investigated by Potentiodynamic polarization. The data revealed that, as the concentration of inhibitors increased from 100 to 500 ppm the inhibition efficiencies increased. The sequence of the inhibition efficiencies increased for the tested compounds arranged as 4, 12b, 8, 14, 10 and 12a respectively. Quantum chemical calculation gives approval to the experimental data and the theoretical data is good agreement with experimental data.

Keywords: Pyrazolo[1,5-a][1,8]naphthyridine, pyrazolo[1,5-a]pyridine, pyrazolo[1,5-a]pyrimidine, 3-amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile, corrosion inhibitor, quantum calculation

1. Introduction
The considerable biological and medicinal activities of condensed pyrazoles initiated considerable recent interest in the development of syntheses of these molecules [1-4]. Pyrazolo[1,5-*a*]pyrimidines can be found in a large number of pharmaceutical agents with a diverse range of activities, and are purine analogues and as such have useful properties as antimetabolites in purine biochemical reactions [5]. Compounds of this class have attracted wide pharmaceutical interest because their antitrypanisommal activity [6], antischistosomal activity [7], activity as HMG-CoA reductase inhibitors [8], COX-2 selective inhibitors [9], AMP phosphodiesterase inhibtors [10], KDR kinase inhibitors [11], selective peripheral benzodiazepine receptor ligants [12] and as antianxiety agents [13]. Recently other pharmaceutical activity has been reported, for example, as an agent for the treatment of sleep disorders [14] and as an oncological agent [15]. Pyrazolo[1,5-a]pyridines are uses as antiherpetics [16].
Organic compounds are famous materials used for inhibition of corrosion specialist the compounds that have heterocyclic atoms N, O, S and P that gives the property of adsorption of the compound [17, 18]. The studied compounds in this work undergoes to heterocyclic compounds. Quantum chemical calculation used to correlate between the experimental and theoretical calculation of compounds. Density function theory (DFT) used for obtain molecular orbitals such as highest occupied molecular orbital E_{HOMO}, lowest unoccupied molecular orbital E_{LUMO} and calculation of energy gap between two energy levels ΔE ($E_{LUMO} - E_{HOMO}$) and these calculation useful for giving indication of stability, activity of compounds [19]. The aim of this work, synthesize new heterocyclic compounds for using as corrosion inhibitor at low concentration reach to 100 ppm up to 500 ppm as maximum concentration used in this study and correlate the results with theoretical calculations.

2. Material and Methods
2.1 Materials
All melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 17,100 FTIR spectrometer as KBr disks. NMR spectra were recorded on a Varian Gemini (400 MHz)

spectrometer with tetramethylsilane (TMS) as an internal standard unless otherwise. Mass spectra were obtained on Finnigan 4500 (low resolution) spectrometers using electron impact (EI). Elemental analyses were carried out in the Micro-analytical Center Cairo University, Giza, Egypt.

2.2 Methods

2.2.1 Synthesis

2,8-Diamino-5-(4-(dimethylamino)phenyl)-6-methylpyrazolo[1,5-a][1,8]naphthyridine-3,4,7-tricarbonitrile 4

Method A: A solution of 3-amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile 1 (1.47g, 10 mmol) and 4-(4-(dimethylamino)phenyl)-2-methylbuta-1,3-diene-1,1,3-tricarbonitrile 2 (2.62g, 10 mmol) in ethanol (50 mL) containing piperidine (0.2 mL) was left under reflux for 4 hr. The solid product obtained on heating was collected by filtration, dried and crystallized from DMF/EtOH 1:1 as yellow crystals. Yield (3.1g, 76.17%), M.p. > 300 °C, FT-IR (KBr, ν, cm^{-1}): 3428,3340,3209 (NH_2), 2220 (C≡N); ^1H NMR (DMSO-*d6*, δ_H, ppm): 2.3 (s, 3H, CH_3), 3.1 (s, 6H, $N(CH_3)_2$), 6.6 (s, 2H, NH_2, D_2O exchangeable), 6.8, 6.9 (d, 2H, Ar-AB), 7.4, 7.5 (d, 2H, Ar-AB), 8.5 (s, 2H, NH_2, D_2O exchangeable); Anal. Calcd. for $C_{22}H_{17}N_9$ (407.16): C, 64.85; H, 4.21; N, 30.94%. Found: C, 64.55; H, 4.07; N, 30.70%.

Method B: A solution of 3-amino-5-(1-cyano-2-(4-(dimethylamino)phenyl)vinyl)-1*H*-pyrazole-4-carbonitrile[20] 5 (2.78g, 10 mmol) and 2-methylpropane-1,1,3-tricarbonitrile, ammonium salt 6 (1.48g, 10 mmol) in ethanol (50 mL) was left under reflux for 4 hr. The solid product obtained on heating was collected by filtration, dried and crystallized from DMF/EtOH 1:1 as yellow crystals. Yield (2.85g, 70.02%), M.p. and mixed M.p. > 300 °C.

2',7'-Diamino-2-oxo-4'*H*-spiro[indoline-3,5'-pyrazolo[1,5-a]pyridine]-3',4',6'-tricarbonitrile 8

A solution of 3-amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile 1 (1.47g, 10 mmol) and 2-(2-oxoindolin-3-ylidene) malononitrile 7 (1.95g, 10 mmol) in ethanol (50 mL) and piperidine (0.2 mL) was left under reflux for 8 hr. The solid product obtained on heating was collected by filtration, dried and crystallized from DMF/EtOH 1:3 as brown crystals. Yield (2.36g, 69.01%), M.p. > 300 °C, FT-IR (KBr, ν, cm^{-1}): 3442,3329,3224 (NH_2, NH), 2217 (C≡N), 1697 (C=O), ^1H NMR (DMSO-*d6*, δ_H, ppm): 6.6 (s, 4H, $2NH_2$, D_2O exchangeable), 7.2-7.5 (m, 4H, Ar), 8.1 (s, 1H, CH-pyridine), 8.4 (s, 1H, NH, D_2O exchangeable); Anal. Calcd. for $C_{17}H_{10}N_8O$ (342.32): C, 59.65; H, 2.94; N, 32.73%. Found: C, 59.39; H, 2.87; N, 32.66%.

2,7-Diamino-5-methylpyrazolo[1,5-a]pyridine-3,4-dicarbonitrile 10

3-Amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile **1** (1.47g, 10 mmol) and ammonium acetate (1.54g, 20 mmol) were mixed with 3-iminobutanenitrile **9** (0.82g, 10 mmol) and the mixture was heated in an oil bath at 140-150 °C for 30 minutes. During this period, ammonia was liberated and the reaction mixture was gradually solidified. After cooling, the solid was treated with ethanol (20 mL), filtered, dried and crystallized from EtOH as yellow crystals. Yield (1.92g, 90.57%), M.p. 304-306 °C, FT-IR (KBr, ν, cm^{-1}): 3421,3305,3217 (NH_2), 3082 (CH, SP^2), 2218 (C≡N); ^1H NMR (DMSO-*d6*, δ_H, ppm): 2.4 (s, 3H, CH_3), 4.4 (s, 2H, NH_2, D_2O exchangeable), 6.3 (s, 1H, CH-pyridine), 8.1 (s, 2H, NH_2, D_2O exchangeable); MS $(EI)^+$:m/z 212 (97.12%) M^+; Anal. Calcd. for $C_{10}H_8N_6$ (212.22): C, 56.60; H, 3.80; N, 39.60%. Found: C, 56.47; H, 3.74; N, 39.45%.

Preparation of compounds 12a,b and 14

General procedure: A solution of 3-amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile 1 (1.47g, 10 mmol) and enaminone 11a or 11b or 13 (which prepared from acetyl acetone or benzoyl acetone or 2,6-diacetyl pyridine with DMFDMA) 10 mmol in ethanol (50 mL) and acetic acid (3 mL) was left under reflux for 6 hr. The solid product obtained after cooling was collected by filtration, dried and crystallized from the proper solvent.

6-Acetyl-2-cyanomethyl-5-methylpyrazolo[1,5-a]pyrimidine-3-carbonitrile 12a

Compound 12a was prepared according to the general method described above using enaminone 11a (1.55g, 10 mmol) and pyrazole 1 (1.47g, 10 mmol). The solid product obtained crystallized from ethanol as brown crystals. Yield (1.85g, 77.41%), M.p. 218-220 °C, FT-IR (KBr, ν, cm^{-1}): 3075 (CH, SP^2), 2964, 2928 (CH, SP^3), 2230 (C≡N), 1688 (C=O), ^1H NMR (DMSO-*d6*, δ_H, ppm): 2.6 (s, 3H, CH_3), 3 (s, 3H, $COCH_3$), 4.5 (s, 2H, CH_2), 7.2 (s, 1H, CH-pyrimidine), MS $(EI)^+$:m/z 239 (5.74%) M^+; Anal. Calcd. for $C_{12}H_9N_5O$ (239.24): C, 60.25; H, 3.79; N, 29.27%. Found: C, 60.08; H, 3.65; N, 29.11%.

6-Benzoyl-2-cyanomethyl-5-methylpyrazolo[1,5-a]pyrimidine-3-carbonitrile 12b

Compound 12b was prepared according to the general method described above using enaminone 11b (2.17g, 10 mmol) and pyrazole 1 (1.47g, 10 mmol). The solid product obtained crystallized from ethanol as orange crystals. Yield (2.2g, 73.09%), M.p. 178-180 °C, FT-IR (KBr, ν, cm^{-1}): 3084 (CH, SP^2), 2937, 2913 (CH, SP^3), 2225 (C≡N), 1659 (C=O), ^1H NMR (DMSO-*d6*, δ_H, ppm): 2.7 (s, 3H, CH_3), 4.6 (s, 2H, CH_2), 7.4- 7.9 (m, 6H, Ar + CH-pyrimidine); Anal. Calcd. for $C_{17}H_{11}N_5O$ (301.31): C, 67.77; H, 3.68; N, 23.24%. Found: C, 67.51; H, 3.55; N, 23.10%.

5,5'-(Pyridine-2,6-diyl)bis(2-(cyanomethyl)pyrazolo[1,5-a]pyrimidine-3-carbonitrile) 14

Compound 14 was prepared according to the general method described above using dienaminone 13 (2.73g, 10 mmol) and pyrazole 1 (2.94g 20 mmol). The solid product obtained crystallized from DMF/EtOH 1:3 as brown crystals. Yield (3.1g, 70.29%), M.p. > 300 °C, FT-IR (KBr, ν, cm^{-1}): 3064 (CH, SP^2), 2914 (CH, SP^3), 2231 (C≡N), ^1H NMR (DMSO-*d6*, δ_H, ppm): 4.5 (s, 4H, $2CH_2$), 8.1- 8.4 (m, 3H, CH-pyridine), 8.9- 9.2 (m, 4H, CH-pyrimidine) ^{13}C NMR (DMSO-*d6*, δ_c, ppm): 17.69, 111.79, 112.58, 116.40, 124.09, 128.06, 138.67, 145.67, 151.29, 152.55, 154.76, 156.79 ; Anal. Calcd. for $C_{23}H_{11}N_{11}$ (441.42): C, 62.58; H, 2.51; N, 34.91%. Found: C, 62.38; H, 2.42; N, 34.77%.

***N'*-(4-Cyano-5-cyanomethyl-1*H*-pyrazol-3-yl)-*N*,*N*-dimethylformimidamide 16**

A solution of 3-amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile 1 (1.47g, 10 mmol) and dimethylformamide dimethyl acetal (1.19g, 10 mmol) in 1,4-dioxane (30 mL) was refluxed for 2h. The solvent was evaporated and the solid product so formed was collected and crystallized from ethanol as yellow crystals. Yield (1.85g, 91.58%), M.p. 175-177 °C, FT-IR (KBr, ν, cm^{-1}): 3168 (NH) 3091 (CH, SP^2), 2960, 2922

(CH, SP^3), 2214 (C≡N), ^{1}H NMR (DMSO-*d6*, δ_H, ppm): 3, 3.2 (2s, 6H, $2CH_3$) 4.1 (s, 2H, CH_2), 8.15 (s, 1H, CH-enamine), 10 (s, 1H, NH, D_2O exchangeable); Anal. Calcd. For $C_9H_{10}N_6$ (202.22): C, 53.46; H, 4.98; N, 41.56%. Found: C, 53.29; H, 4.85; N, 41.40%.

1,2,3,5,6-Pentaazaacenaphthylene-5,7(1*H*)-diamine 17

A solution of enamine 16 (2.02g, 10 mmol) in ethanol (20 mL) containing hydrazine hydrate (0.6 mL) was refluxed for 6h. The solid product which formed on heating was collected by filtration, dried and crystallized from DMF/EtOH 1:3 as brown crystals. Yield (1.22g, 64.55%), M.p. > 300 °C, FT-IR (KBr, ν, cm^{-1}): 3304,3193 (NH_2, NH), ^{1}H NMR (DMSO-*d6*, δ_H, ppm): 5.1 (s, 2H, NH_2, D_2O exchangeable), 5.5 (s, 2H, NH_2, D_2O exchangeable), 6.1 (s, 1H, CH-pyridine), 8.2 (s, 1H, CH-pyrimidine), 9 (s, 1H, NH, D_2O exchangeable); Anal. Calcd. for $C_7H_7N_7$ (189.18): C, 44.44; H, 3.73; N, 51.83%. Found: C, 44.28; H, 3.61; N, 51.66%.

7-Amino-2-(cyanomethyl)pyrazolo[1,5-a]pyrimidine-3,6-dicarbonitrile 18

A solution of enamine 16 (2.02g, 10 mmol) and malononitrile (0.66g, 10 mmol) in ethanol (30 mL) containing piperidine (0.2 mL) was refluxed for 6h. The solid product which formed after cooling was collected by filtration, dried and crystallized from ethanol as orange crystals. Yield (1.51g, 67.71%), M.p. 295-297 °C, FT-IR (KBr, ν, cm^{-1}): 3347,3187 (NH_2), 2220 (C≡N), ^{1}H NMR (DMSO-*d6*, δ_H, ppm): 4.4 (s, 2H, CH_2), 6.25 (s, 2H, NH_2, D_2O exchangeable), 7.4 (s, 1H, CH-pyrimidine); Anal. Calcd. for $C_{10}H_5N_7$ (223.20): C, 53.81; H, 2.26; N, 43.93%. Found: C, 53.67; H, 2.17; N, 43.75%.

2.2.2 Corrosion cell

The corrosion cell consists of three electrodes, mild steel as working electrode, saturated calomel electrode as reference electrode and platinum wire as counter electrode. Three electrodes immersed in corrosive media of 1.0 M H_2SO_4 in absence and presence of different inhibitors at 500 ppm concentration. Mild steel constituent's % Fe as 98.91 which supplied from AL - EZZ Company in Alexandria. Mils steel electrodes were prepared by polishing it with SiC paper up to 1200 grade.

2.2.3 Electrochemical techniques

Electrochemical techniques applied for corrosion rate of mild steel electrodes exposed to corrosive media in absence and presence of tested inhibitors. The electrochemical techniques are open circuit potential, polarization techniques such linear polarization and Tafel polarization.

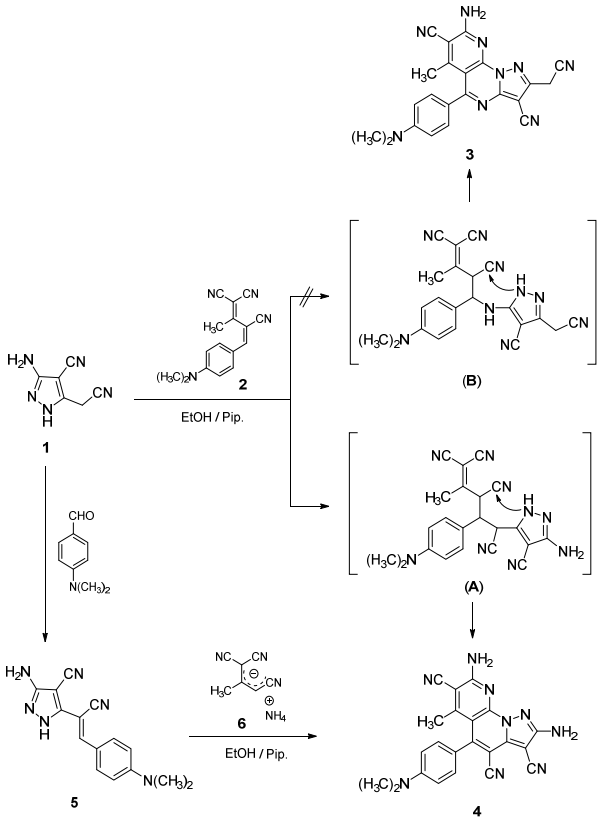
2.2.4 Quantum chemical calculations

DFT/B3LYP has been widely used in the description of the inhibitor metal surface mechanism and is also recommended for the study of chemical reactivity and selectivity of molecules [21]. In the present study calculations were performed using Gauss View 5.0 with Gaussian 09W program package [22] Geometry optimizations were conducted by DFT using Becke's three parameter exchange functional (B3 LYP) [23, 24] and the 6-3111G (d,p) basis set [25].

The parameters obtained from quantum calculation represented as the energies of the highest occupied molecular orbital E_{HOMO}, energy of the lowest unoccupied molecular orbital E_{LUMO}, the energy gap E_{LUMO} - E_{HOMO} of tested compounds.

3. Result and Discussion

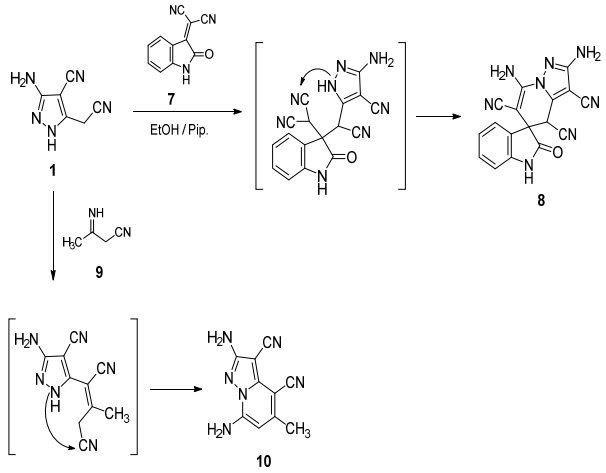
The 3-Amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile 1 was prepared following the procedure described by Edward *et at* [26]. The behavior of 3-amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile 1 towards some electrophiles such as arylidens, enamines and DMFDMA is reported. Reaction of 3-amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile 1 with 4-(4-(dimethylamino) phenyl)-2-methylbuta-1,3-diene-1,1,3-tricarbonitrile 2 in ethanol containing piperidine afforded pyrazolo[1,5-a][1,8]naphthyridine derivative[27] 4. The other possible structure 3 was discarded on the basis of spectral data. ^{1}H NMR spectrum of compound 4 exhibits the absence of methylene protons and showed the presence of signal of $N(CH_3)_2$ moiety at δ_H 3.1 ppm and two singlet signals at δ_H 6.6, 8.5 ppm corresponding to two amino groups. The formation of 4 is assumed to proceeds *via* Michael adduct (A) followed by intramolecular cyclization and aromatization to afford compound 4. Compound 4 can be obtained from other methed by the reaction of pyrazole 1 with 4-(dimethylamino)benzaldehyde to yield arylidene 5 followed by reaction with 2-methylpropane-1,1,3-tricarbonitrile, ammonium salt 6 to afford compound 4 (scheme 1).



Scheme 1: Synthesis of pyrazolo[1,5-a][1,8]naphthyridine 4

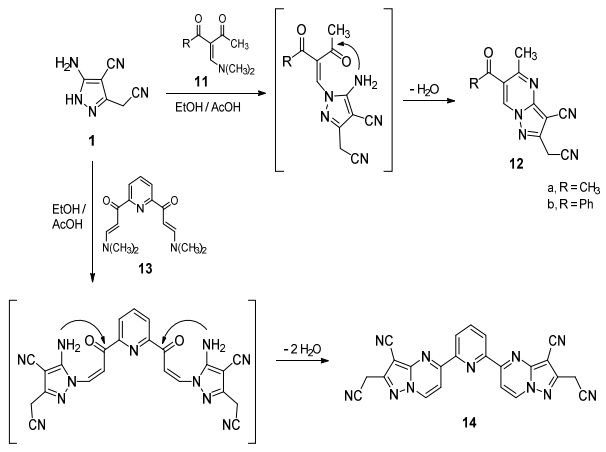
Also, pyrazole 1 reacted with 2-(2-oxoindolin-3-ylidene)malononitrile 7 to give spiro compound 8 *via* Michael addition of methylene group of pyyazole 1 to olefinic double bond of compound 7 followed by nucleophlic cyclization to form spiro compound 8. Pyrazolo[1,5-a]pyridine derivative 8 was confirmed by spectral data as well as elemental analysis, IR spectrum of compound 8 shows bands for amino, cyano and carbonyl groups. Also, ^{1}H NMR spectrum of compound 8 exhibits signals of amino and aromatic protons beside singlet signal at δ_H = 8.1 ppm corresponding to CH-pyridine. In continuation of nucleophilic reactions, 3-amino-5-

cyanomethyl-1*H*-pyrazole-4-carbonitrile 1 reacts with 3-iminobutanenitrile 9 in the presence of ammonium acetate to afford pyrazolo[1,5-a]pyridine derivative 10. This reaction proceeds *via* elimination of ammonia molecule followed by nucleophlic cyclization to form compound 10 (scheme 2). ^{1}H NMR spectrum of compound 10 exhibits singlet signal for CH-pyridine at δ_H = 6.3 ppm, IR spectrum exhibits the same group (CH, SP^2) at ν_{max} 3082 cm^{-1}.



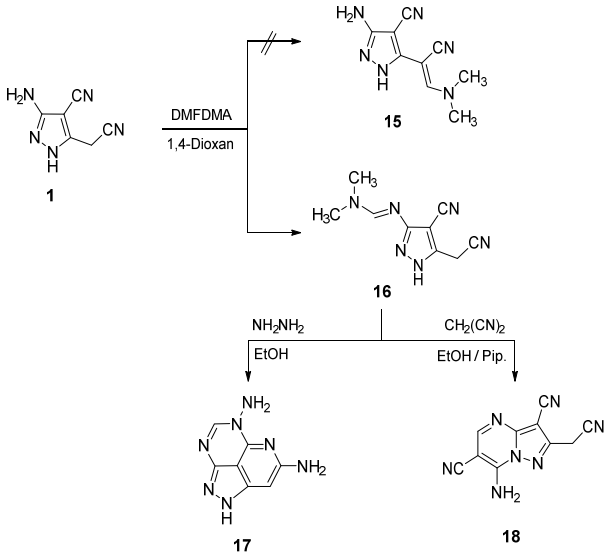
Scheme 2: Synthesis of pyrazolo[1,5-a]pyridines 8 and 10

3-Amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile 1 contains amino group as another nucleophilic center. The nucleophlicty of amino group can be investigated towards enaminones [28, 29] 11a,b and 13 in acid medium to give pyrazolo[1,5-a]pyrimidine derivatives 12a,b and 14 respectively. Pyrazolo[1,5-a]pyrimidine derivatives which obtained from this reaction can be established by spectral data as well as elemental analysis, IR spectra of these compounds exhibit disappearance of NH_2 and NH groups, also, disappearance of carbonyl group from compound 14. ^{1}H NMR spectra show signals of active methylene proton at about δ_H 4.5 ppm and absence of any signals to NH_2 and NH protons. The mechanism of formation of pyrazolo[1,5-a]pyrimidine derivatives 12a,b and 14 proceeds *via* nucleophlic attack of NH group of pyrazole 1 to double bond of enaminones 11a,b and 13 followed by nucleophlic intramolecular cyclization and elimination of water molecule (scheme 3).



Scheme 3: Synthesis of pyrazolo[1,5-a]pyrimidines 12 and 14

Our investigation was extended to study the behavior of 3-amino-5-cyanomethyl-1*H*-pyrazole-4-carbonitrile 1 towards dimethylformamid dimethyl acetal (DMFDMA). So that, when react 1 mol of DMFDMA with pyrazole 1 in 1,4-dioxan, afforded enamine 16. The other possible structure 15 was ruled out on the basis of spectral data. IR and ^{1}H NMR spectra of this product show the absence of amino group, this indicates that the reaction proceeds *via* amino group and the reaction product fit structure 16 not 15. Also, ^{1}H NMR spectrum of compound 16 shows signals at δ_H = 3, 3.2 and 8.15 ppm corresponding to $N(CH_3)_2$ moiety and CH-enamine respectively. The reaction of compound 16 towards nucleophiles such as hydrazine hydrate and malononitrile can be investigated, so refluxing of compound 16 with hydrazine hydrate afforded tricyclic compound 17 while, reaction of compound 16 with malononitrile afforded pyrazolo[1,5-a]pyrimidine derivative 18 (scheme 4). The compounds 17 and 18 can be established by spectral data as well as elemental analysis. IR spectra of these compounds show the appearance of amino group, also, ^{1}H NMR spectra of these compounds show absence of $N(CH_3)_2$ moiety and the appearance of amino group.



Scheme 4: Synthesis of tricyclic compound 17 and pyrazolo[1,5-a]pyrimidine 18

Electrochemical chemical techniques

Open circuit potential is the relation between potential against time at zero current, Fig (1) presented the relation between E (mV) vs saturated calomel electrode (SCE), its clear from fig that open circuit potential shift toward more positive value at presence of different inhibitors than its absence (1.0M H_2SO_4), that due to presence of passive layer of tested compounds on the surface of mild steel electrodes. The data tablet in Table(1), it is clear the potential of steady state potential of blank solution 1.0M H_2SO_4 shift toward positive direction from 1.0M H_2SO_4 (- 487mV) to (-467mV, - 455mV, - 456mV, - 462mV, - 486mV and - 476mV), for the compounds (8, 10, 12a, 4, 12b and 14), respectively.

Potentiodynamic polarization

Potentiodynamic polarization is method for corrosion rate calculation, calculation of corrosion rate and inhibition efficiency calculated from equations (1 and 2)

Corrosion rate = 0.13 ×Icorr.×eq. wt of metal used / A×D of metal used……..(1)
Where, 0.13 is constant, Icorr is corrosion current, Eq. wt. is equevelant weight of tested metal, A is area exposed to study and D is density of used metal.

Inhibition efficiency IE% = (CR uninh. – CR inh.) ×100/ CR uninh…… [30] **(2)**
Where, CR uninh. is corrosion rate of metal exposed to blank without inhibitor
CRinh. is corrosion rate of metal in presence of inhibitor.
Tafel polt polarization parameters such as corrosion current Icorr, corrosion rate CR and inhibition efficiency IE% were calculated and presented in Table (1) and Fig (2), its observed from tablet data the Icorr of blank reach to 2750 µA\Cm^2 and with add the inhibitors at 500ppm the Icorr decreased to reach 535 µA\Cm^2 for compound 4.
Generally, at 500 ppm of different compounds used in this study the sequence of increasing IE% in the direction 4>12b> 8>14>10 more than 12a.

Quantum chemical calculation
Quantum calculation parameters such as E_{HOMO}, E_{LUMO} and energy gap (ΔE) illustrated in Table (2), it's clear from data there are correlation between theoretical and experimental calculation of mild steel exposed to corrosive media in absence and presence inhibitors. Fig. (3) shows optimized structures of tested compound, its HOMO and LUMO shapes. Energy gap is indication of activity or stability of compounds, where, as the low value of energy gap give the compound activity hence the low gap energy between HOMO and LUMO energy. From data there is a good agreement between theoretical and experimental data and it presented as follow
Experimental IE% in the direction 4>12b> 8>14>10 more than 12a on the other hand the activity of tested compounds arranged as the same direction of experimentally data

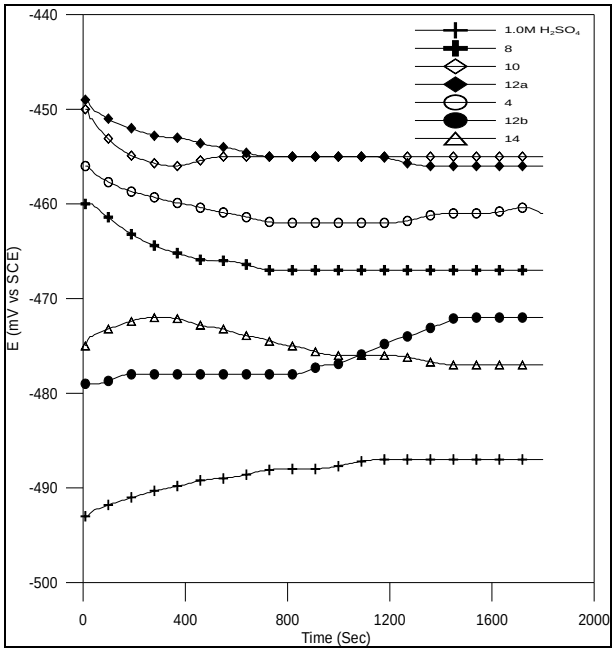


Fig 1: Potential (mV) versus time (Sec) for mild steel electrodes at presence and absence of tested inhibitors.

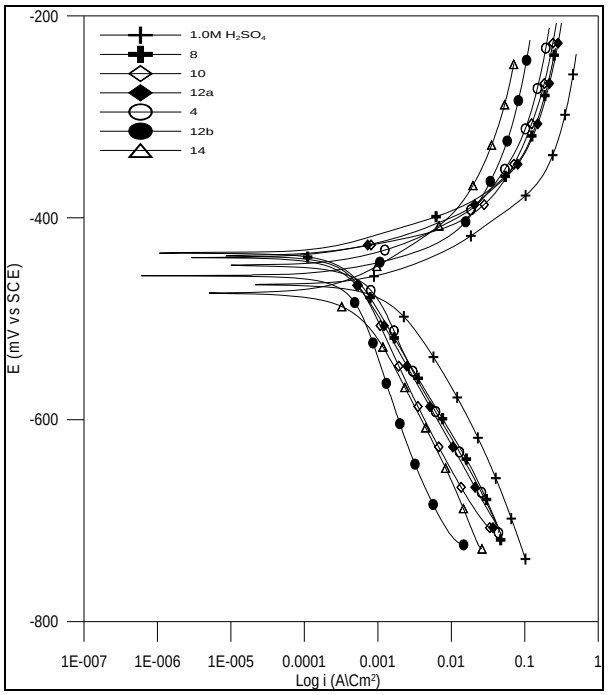


Fig 2: Tafel plot polarization of tested compounds for mild steel at exposed to 1.0M H_2SO_4

Table 1: E im, Es.s potentials and Potentiodynamic parameters of tested compounds for mild steel exposed to 1.0 M H_2SO_4

Inhibitor	-Eim	-Es.s	Icorr	CR	IE%
1.0M H_2SO_4	493	487	2750	2535.60	
8	460	467	750	691.53	73
10	450	455	800	737.63	71
12a	449	456	870	802.17	68
4	456	462	535	493.29	81
12b	483	486	690	617.76	76
14	475	476	780	719.19	72

Table 2: Quantum chemical calculation parameters of tested compounds

Compound	E_{HOMO}	E_{LUMO}	Energy gap ΔE
8	-0.2976	-0.1966	0.101
10	-0.3024	-0.1832	0.1192
12A	-0.326	-0.2015	0.1245
4	-0.3014	-0.2187	0.0827
12B	-0.325	-0.2242	0.1008
14	-0.3228	-0.2181	0.1047

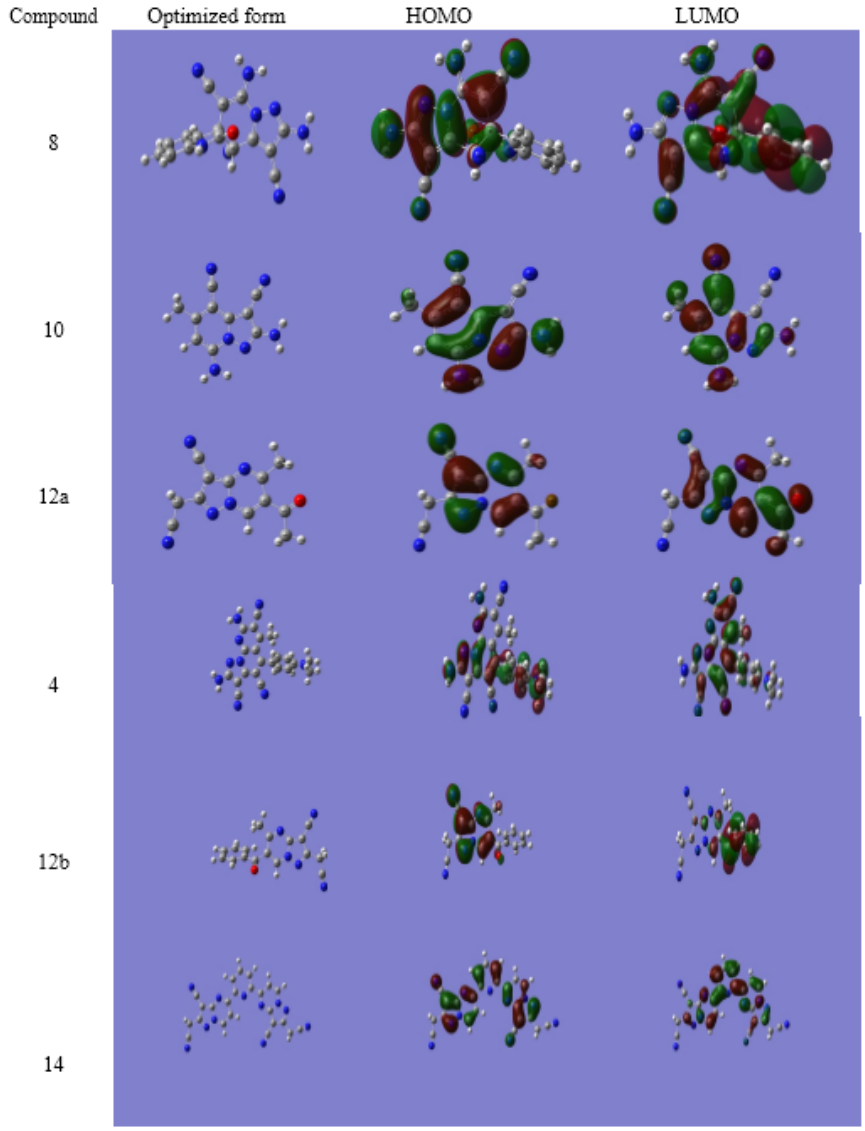


Fig 3: The optimized molecular structure (HOMO) and (LUMO) of the investigated compounds using DFT/ B3LYP/ 6-311G(d,p) basis set method

4. Conclusion

This work shows that the synthesized compounds pyrazolo[1,5-a][1,8]naphthyridine, pyrazolo[1,5-a]pyridine and pyrazolo[1,5-a]pyrimidine derivatives can work as good corrosion inhibitors with the maximum inhibition in around 81%, corresponding to the optimum concentration at 500 ppm for corrosion mild steel surface in 1.0 M H_2SO_4.

Theoretical chemical calculations showed a good correlation between theoretical chemical parameters for the studied compounds and their % IE for the corrosion process in agreement with experimental results.

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6. References

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