New derivative of 1,2-Dihydropyridine-3-Carbonitrile as Corrosion Inhibitor

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Abstract
New 1,2-dihydropyridine-3-carbonitrile derivative compound as corrosion inhibitor namely, 3,3’-(3,3’-(1E,1’E)-1,4-phenylenebis(diazene-2,1-diyl)bis(4-(dimethylamino)-3,1-phenylene))bis(2-oxo-6-(2,4,6-trihydroxyphenyl)-1,2-dihydropyridine-3-carbonitrile) (PDPTD) was synthesized by cyclization of compound (1) with 1-(2,4,6-trihydroxyphenyl) ethenone in presence of ethyl cyano acetate and ammonium acetate. The new synthesized compound has been characterized using Melting point, FT-IR spectroscopy and 1H-NMR. The new synthesized compound (PDPTD) has been tested on mild steel (MS) in 1 M HCl media by a weight loss method and identification of the surface technique employed by scanning electron microscope (SEM) studies. The weight loss investigation demonstrated that inhibition performances have been improved via concentration raising of inhibitor. To support our results scanning electron microscopy has employed about clarify the surface from the MS with and without (PDPTD) in 1.0 M HCl media. The inhibition performance rate was 83% at the maximum utilized concentration of (PDPTD).

Keywords: benzene-1,4-diamine; 4-(dimethylamino)benzaldehyde; SEM.

1. Introduction
Pyridine derivatives are the majority important heterocycles which found in medicinal chemistry such they have been an excellent biological activity for a wide range from applications, including antimicrobial [1], antiinflammatory [2], anti-HIV [3], antiplasmodial [4], antituberculal [5], antibacterial [6], anticonvulsant [7], COX inhibitor [8], anticancer effects [9], blood platelet aggregation inhibitors [10], antioxidant [11], antitumor [12] and antifungal activities [13]. The Corrosion inhibitor is a...
substance which has retarded that inhibitors function at one either more ways about control corrosion: through adsorption from a thin film at the surface from a corroding material, through inducing the formation from a thick corrosion creator, or through changing the characteristic from the environment resulting at reduced offensive [14]. The Corrosion is a natural process, which changes a refined metal about a more chemically-stable shape, like its oxide, hydroxide, or sulfide. It has been the gradual demolition from materials (customarily metals) through chemical and/or electrochemical reaction for their medium. The Corrosion engineering is the field appropriated about controlling and pausing corrosion. The use from chemical inhibitors about diminish the rate from corrosion processes has been quite varied. At the oil extraction and making industries, inhibitors have constantly considered about the first line from protect against corrosion. A large number from scientific studies have devoted about the subject from the corrosion inhibitors [15]. The Corrosion inhibitors have been one from the practical and have cost efficient methods from controlling metallic corrosion. They have been inorganic either organic substances. Inorganic substances appropriate such metal corrosion inhibitor must simply oxidize the metal about form an inefficient layer which prevents immediate ions-metal interaction and hence prevent the rate from metal dissolution at the medium. The organic accordance, on the another hand, must own features containing presence from heteroatoms and/or double bonds, big surface area, efficient centre, etc. which at adsorption to the metal surface will be blanket a big area from the metal and so isolate it of the offensive ions present at the medium[16].

The aim of this work is to about study the inhibiting effect from 3,3′-(3,3′-(1E,1'E)-1,4-phenylenebis (diazene-2,1-diyl)bis(4-(dimethylamino)-3,1-phenylene))bis(2-oxo-6-(2,4,6-trihydroxyphenyl)-1,2-dihydropyridine-3-carbonitrile) (PDPTD) at mild steel at one normal hydrochloric acid solution. The results were supplemented by SEM, IR and NMR studies. Suggested structure for combined consumption inhibitor is appeared as shown in Figure (1).
2 Experimental

2.1 Synthesis of corrosion Inhibitor:

2.1.1 Synthesis of Azo Derivative (1)

Benzene-1,4-diamine (0.01 mole) was added to a mixture of water (4 ml) and concentrated hydrochloric acid (4.5 ml). The resulting solution was stirred for 10 min., before being cold to (0-5) °C. A solution of sodium nitrite (1.38g.,0.02 mole) in water (2.5 ml) is added dropwise \[17\], after being stirred for 10 min. The resulting solution of diazonium salt was added dropwise to a mixture of 4-(dimethylamino)benzaldehyde (2.98g., 0.02 mole) in ethanol and 10% NaOH (20ml.)at (0-5)°C at pH=5.5 and the disappearance of reactants was figured according to Thin-layer chromatography (TLC) technique. After the addition was completed, the mixture was stirred for further 20 min., then it left for 1 hr. The resulting solid was filtered off, dried and recrystallized from ethanol to get the compound (1), red precipitate ,yield 84%, M.P (80-82°C).
2.1.2 Synthesis of PDPTD (2)
A solution of compound (1) (0.001 mole) in ethanol (10 ml.), 1-(2,4,6-trihydroxyphenyl) ethanone (0.002 mole), ethyl cyano acetate (0.226g., 0.002 mole), ammonium acetate (1.2g., 0.016 mole) were added [18]. The reaction mixture was refluxed for 2hrs and the disappearance of reactants was figured according to TLC technique. The consequent formed has filtered off then washed by water, dried and recrystallized of ethanol to get the target compound (2), yellow precipitate, yield 68%, M.P (112-115°C).

2.2 Corrosion technique:
2.2.1 MS specimens
MS specimens got by the Metal Samples Company were employed all through this investigation. The formation (wt %) from the mild steel had been as follows: iron, 99.21; carbon, 0.21; silicon, 0.38; phosphorous, 0.09; sulfur, 0.05; manganese, 0.05; and aluminum, 0.01. The specimen was cleaned in accordance with procedure G1-03 that mentioned in reference [19]. The measurements were conducted in aerated [20]. The components were analyzed in Malaysia by UKM University with X-Ray Fluorescence, without stirring 1.0 M HCl solutions including different concentrations from (PDPTD) compound.

2.2.2 Technique of Weight Loss
Compounds in duplicate were suspended in 200 mL of the examine media, with & without the PDPTD (2) corrosion Inhibitor of different concentration (0 mM, 0.1 mM, 0.15 mM, 0.2 mM, 0.25 mM, 0.5 mM), for 1, 2, 24, 48 and 72 hrs. at room temperature [21], Specimens weights before/after immersed were computed. The inhibition efficiency of the mild steel was determined by using the average of the duplicated value using the equation [22]:

\[
\text{Inhibition Efficiency (IE \%) = \left(1-\frac{W_2}{W_1}\right) \times 100}
\]

Where, W1 and W2 are damage weight from Mild Steel (MS) without and with (PDPTD) (2).

3. Results and Discussion
3.1 Identification of PDPTD (2)
The synthesis of an azo dye needs two organic compounds a diazonium salt and a coupling component. The diazonium salt like an electrophile interacts with an electron-rich coupling component, as a phenol derivative over an electrophilic aromatic substitution reaction. The FTIR spectrum of compound (1) has showed an absorption band at (2906 cm⁻¹) because of stretching vibration for C-H arom., band at (2820,2804) for C-H aliph., band at (1737 cm⁻¹) because of stretching vibration at C=O of aldehyde, band at (1541 cm⁻¹) indicating the (N=N).

The inhibitor 3,3'- (1E,1'E)-1,4-phenylenebis (diazene-2,1-diyl)bis (4 (dimethylamino)-3,1-phenylene)bis (2-oxo-6-(2,4,6-trihydroxyphenyl)-1,2 dihydropyridine-3-carbonitrile) (PDPTD) was prepared in good yield by reflection reaction of compound (1) and 1-(2,4,6-trihydroxyphenyl)ethanone. The compound (2) was identified by FTIR and ¹HNMR spectroscopy. The FTIR spectrum of the compound (2) shows bands at the frequency of (1705 cm⁻¹) owing to the carbonyl group from amide appears, the NH near (3150) cm⁻¹. And the appearance from absorption band during (2208.5) cm⁻¹ for CN group. The ¹HNMR spectrum of compound (2) shows the following data: 3.09 (s,12H,N(CH₃)₂), 6 (s,2H, C=CH for pyridinone ring), 7.1- 7.8 (m,14H,Ar-H), 8 (s,2H, NH), 10 (s, 2H, -OH), and 11.9 (s, 4H, -OH).
Figure 2. The FTIR spectrum of compound (1).

Figure 3. The FTIR spectrum of compound (2).
3.2 Technique of Weight Loss (Concentration Effect)

The inhibition efficiency (IE) estimates computed from weight reduction estimations for MS in the corrosive mixture that contain different concentrations of PDPTD (2) at encompassing temperature are appeared in Figure (4), that the PDPTD diminished the corrosion from MS in corrosive especially. The IE% expanded with a rise in concentration of PDPTD (2) and attained upper IE at 0.5 mM concentration from PDPTD. The raising in IE% for raise at concentrations were promoted from the raise at the extent from performance of PDPTD preservation. The inhibition efficiency from inhibitor into the corrosion from steel has obtained by using the following equation [23]:

\[
\text{Inhibition Efficiency (IE \%) = (1-W_{corr}/W°_{corr}) \times 100}
\]

Wcorr and W°corr are the corrosion rate from steel samples with and without the inhibitor.

The best of inhibitor efficiency has been given 83% which agree to 0.5 mM concentration of PDPTD in 1.0M HCl at 72 hours.

| Concentration of PDPTD | %IE at 1hr. | %IE at 3 hr. | %IE at 24 hr. | %IE at 48 hr. | %IE at 72 hr. |
|------------------------|-------------|--------------|---------------|---------------|---------------|
| 0 mM                   | 0.00        | 0.00         | 0.00          | 0.00          | 0.00          |
| 0.1 mM                 | 0.00        | 0.1          | 0.47          | 2.3           | 3.46          |
| 0.15 mM                | 0.01        | 0.14         | 1.43          | 7             | 12            |
| 0.2 mM                 | 0.03        | 0.35         | 3             | 15            | 32            |
| 0.25 mM                | 0.04        | 0.4          | 4.5           | 21            | 51            |
| 0.5 mM                 | 0.05        | 1.2          | 12            | 42            | 83            |

Figure (4) shows the graph of percentage inhibitor efficiency against inhibitor concentration into several time for PDPTD (2) respectively, the results of the experiment have shown that PDPTD (2) reduced the corrosion rate to 83 % into this study. The inhibitor efficiency has been encouraging and this can be used at the industries such a substitute into the significant chemical inhibitors.

![Figure 4. Different concentrations of PDPTD vis different immersion periods time for Inhibition Efficiency (IE %) of mild steel.](image)
3.3. Scanning Electron Microscopy (SEM) Analysis

SEM analysis had performed about discuss the surface morphology from the mild steel after inundation at 1.0 M HCl at the absence and the presence from PDPTD, Figure (5). Destroyed surface had observed at the absence from PDPTD because of high dissolution rate from iron by such pH, yet a thin and uniform layer during the metal surface had observed at the presence from PDPTD (2), the cracks at the film have been because from the dehydration from surface ago the surface had dried previously the SEM portrait. This was proof that PDPTD had absorbed by the mild steel surface and insulates the surface of the acidic intermediate [24].

![Figure 5. The SEM pictures, of MS in solution of HCl without PDPTD (2).](image1)

![Figure 6. SEM picture, for MS in solution of HCl with PDPTD (2).](image2)
3.4. PDPTD (2) as Inhibitor- Action Mechanisms

Mostly inhibitors have adsorbed at the mild steel and structures a paint film neither a synthetic bonds structure through restraint from inhibitor and metal and of inorganic complex (free electrons from inhibitor-ligand for the unoccupied d-orbital into the metal). The action mechanism from PDPTD (2) such inhibitor can move ahead through means from interaction. Interaction of PDPTD (2), metal electrostatically neither interaction from unpaired electrons from hetero-atoms from PDPTD (2) for metal. IE from PDPTD (2) has been demonstrated about the hetero-atoms, charge, size, stereo-hindrance and ability from consistence from metallic insoluble complex. PDPTD (2) work like bi-dentate ligand unpaired electrons from oxygen and nitrogen about compose coordinated bonds for metal Figure (7).

![Figure 7. The suggested mechanism of PDPTD (2) as corrosion inhibitor](image)

4. Conclusions

3,3′-(3,3′-(1E,1'E)-1,4-phenylenebis(diazene-2,1-diyl)bis(4(dimethylamino)-3,1-phenylene))bis(2-oxo-6-(2,4,6-trihydroxyphenyl)-1,2 dihydropyridine-3-carbonitrile) as new inhibitor for surface of mild steel was prepared compound (1) and the structure of its molecule was identified based on NMR and FT-IR spectroscopy. The results of this investigations revealed that the prepared 1,2-Dihydropyridine-3-Carbonitrile derivative namely PDPTD worked as an excellent corrosion inhibitor in corrosive media for surface MS in solution of HCl with concentration subordinate mode. The inhibition performance of PDPTD as an inhibitor most extreme hindrance proficiency was up to 83% at 0.5 mM PDPTD concentration. PDPTD (2) shows the productive natural inhibitor having great inhibitive characteristics because of quality of atoms namely nitrogen with oxygen. SEM estimations bolstered development of a defensive layer through PDPTD (2) on the MS surface. The anti-corrosion investigation for PDPTD (2) showed the protection of surface of MS in corrosive solution.

Acknowledgements

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References

[1] Gaonkar S L, Rai K M L and Prabhuswamy B 2007 Med. Chem. Res. 15 407–417
[2] Hosni H M and Abdulla M M 2008 Acta Pharm. 58 175–186
[3] Ali M A, Yar M S, Siddiqui A A, Sriram D, Yogeeswari P and de Clercq E 2007 Acta Pol. Pharm. 64 423–428
[4] Kumar S, Das S K, Dey S, Maity P, Guha M, Choubey V, Panda G and Bandyopadhyay U 2008 Agents Chemother. 52 705–715
[5] Lourenço M C S, de Souza M V N, Pinheiro A C, de Lima Ferreira M, Goncalves R S B, Nogueira T C M and Peralta M A 2007 ARKIVOC p 181–191
[6] Sharma P C and Jain S 2008 Acta Pol. Pharm. 65 551–556
[7] Shafiee A, Rastkari N and Sharifzadeh M 2004 Dari 12 81–86
[8] Chintakunta V K, Akella V, Vedula M S, Mannoor P K, Mishra P, Casturi S R, Vangoori A and Rajagopalan R 2002 Eur. J. Med. Chem. 37 339–347
[9] Thapa P, Karki R, Thapa U, Jahng Y, Jung M J, Nam J M, Na Y, Kwon Y and Lee E-S 2010 Bioorg. Med. Chem. 18 377–386
[10] Sotelo E, Fraiz N, Yanez M, Terrades V, Laguna R, Cano E and Ravina E 2002 Bioorg. Med. Chem. 10 2873–2882
[11] Caliskan E B, Sukuroglu M, Coban T, Banoglu E and Suzen S 2008 J. Enz. Inhib. Med. Chem. 23 225–229
[12] Zhang S-X, Bastow K F, Tachibana Y, Kuo S-C, Hamel E, Mauger A, Narayanan V L and Lee K H 1999 J. Med. Chem. 42 4081–4087
[13] Wu J, Kang S, Luo L, Shi Q, Ma J, Yin J, Song B, Hu D and Yang S 2013 Chem. Cent. J. 7 64
[14] Khaled K F 2003 Electrochimica Acta 48 2493-2503
[15] Jones L W 1988 Corrosion and Water Technology for Petroleum Producers, Tulsa, Okla, Oil and Gas Consultants International
[16] Lebe A, Israel O and Emeka E 2014 International Journal of Materials Engineering 4 171-179
[17] Gupta P, Gupta JK and Halve AK 2014 Int J Res Pharm Sci 4 13-20
[18] Beheshhtia Y, Khoshidi M, Heravi M and Baghernejad B 2010 Eur. J. Chem. 1 232-235
[19] ASTM G1-3 2003 Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens. ASTM International: (West Conshohocken, PA, USA)
[20] Al-Amiery AA, Al-Majedy YK, Kadhum AAH, Mohamad AB 2016 Res Chem Intermed 42 3905-3918
[21] Salami L, OP Akinyemi, RJ Patinvoh 2012 Global Engineers and Technologists Review 2 1-6
[22] Aytac A and Ozmen M 2005 Mater. Chem. Phys. 89 176-181
[23] Touir R, Dhikireche N, Ebn Touhami M, Sfaira M, Senhaji O, Robin J J, Boutevin B, Cherkaoui M 2010 Mat. Chem. Phys. 122 1-9
[24] Sokolova V and Anna-Kristin 2011 Biointerfaces 87 146-150