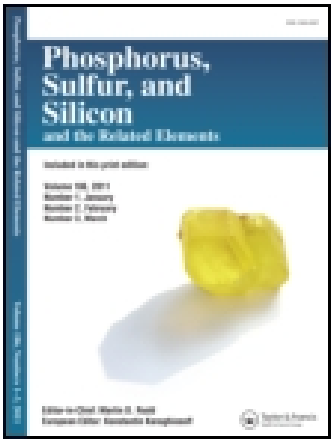

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Synthesis and Surface Characterization Studies of Polyether-Linked Symmetric Higher Sulfanyl-1,3,4-Oxadiazoles

A. Yıldırım[a] & S. Öztürk[a]

[a] Department of Chemistry, Uludağ University, Bursa, Turkey

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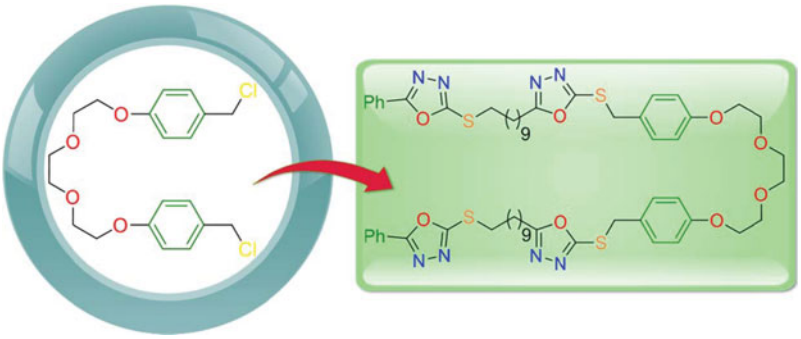
A. Yıldırım and S. Öztürk
Department of Chemistry, Uludağ University, Bursa, Turkey

GRAPHICAL ABSTRACT



Abstract *The synthesis and the characterization of a series of novel symmetric double length alkyl-chained sulfanyl-1,3,4-oxadiazoles functionalized with a polyether head group are reported. In addition, surface characterization studies were conducted on the metal surface of these synthesized compounds. The metal surfaces were characterized by contact angle measurements via the sessile-drop method, and 3D images of the metal surface were obtained using an optical profilometer. The surface studies showed that the inhibitor molecule increases the hydrophobic character and decreases the wettability of the metal surface.*

Keywords Oxadiazoles; semi-crown ethers; surface characterization

INTRODUCTION

N-Acylhydrazines are useful materials for a number of biological properties and are also important building blocks for a wide range of heterocyclic products. A large number of compounds derived from hydrazide or *N*-acylhydrazine groups have been reported as active biological entities, where 1,3,4-oxadiazole-2(3*H*)-thiones and some of their substituted analogues play a vital biological role because of their wide range of therapeutic activities, such

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Address correspondence to Dr. A. Yıldırım PhD, Uludağ University, Chemistry, Görükle Kampüs, Bursa 16059, Turkey. E-mail: yildirim@uludag.edu.tr
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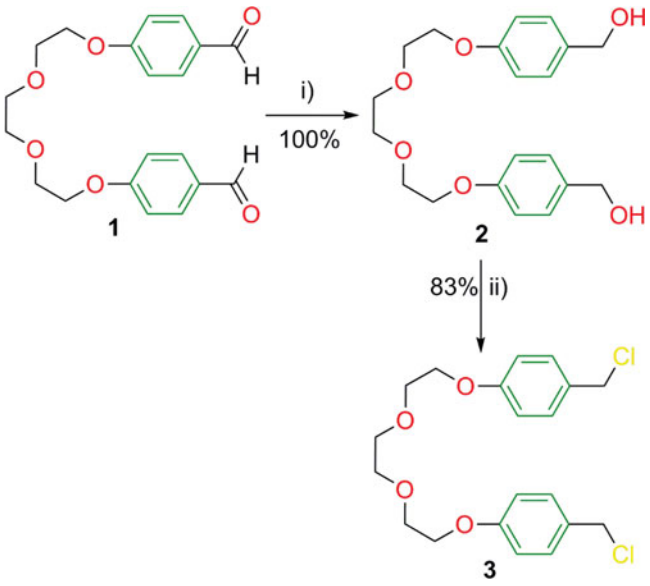
as fungicidal,[1] anti-inflammatory,[2,3] antimicrobial,[4] anticonvulsant,[5] and antitubercular,[6] and they also function as noncompetitive nucleotide pyrophosphatase/phosphodiesterase 1 inhibitors.[7] Furthermore, a common route for the preparation of triose and pentose derivatives as models for acyclic C nucleosides has been reported.[8] These compounds have also demonstrated the ability to protect metals against acidic corrosion.[9,10] In the present study, compounds with a long hydrocarbon tail group were chosen as a corrosion inhibitor because of their good film-forming properties on the metal surface and that the long hydrocarbon tail plays an important role in the mechanism of corrosion inhibition. This tail has a strong tendency for self-assembly in forming a highly hydrophobic barriers for water. Thus the contact angle measurements of mineral oil-water system indicated that the surface became highly hydrophobic. The common synthetic approach for sulfanyl-1,3,4-oxadiazoles involves the cyclization of carbodithioates to yield the corresponding 1,3,4-oxadiazole-2(*H*)-thione or 2-mercapto-1,3,4-oxadiazole intermediates[11–15] followed by reacting these intermediates with a suitable halide compound under various basic conditions. In this study, various polyether-linked 1,3,4-oxadiazoles were designed and synthesized and surface characterization studies were also performed.

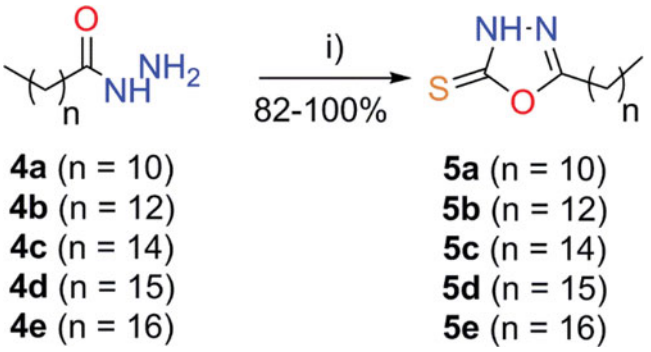
RESULTS AND DISCUSSION

Chemical Synthesis

The starting bis-aldehyde **(1)** was prepared according to the methods given in the literature.[16,17] Compound **(1)** was reduced with $NaBH_4$ to yield the corresponding bis benzyl alcohol **(2)**[18,19] quantitatively as a pure product. After the treatment of **(2)** with $SOCl_2$, an 83% yield of bis-benzyl chloride **(3)**[18,19] (Scheme 1) was obtained.

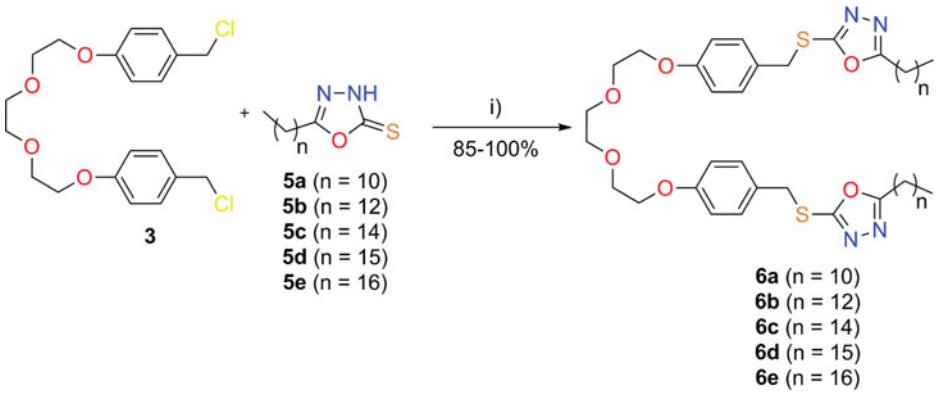


Scheme 1 Reagents and conditions: (i) $NaBH_4$, EtOH/THF, 0°C–r.t., 1 h; (ii) $SOCl_2$, 1,4-dioxane, r.t., 48 h.



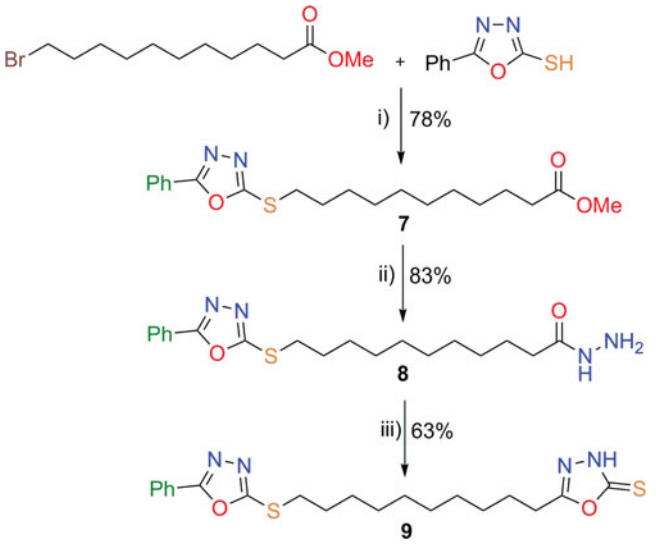
Scheme 2 Reagents and conditions: (i) CS_2, KOH, EtOH, reflux, 24 h.

For the preparation of the starting *N*-acylhydrazines **4a** ($n = 10$), **4b** ($n = 12$), **4c** ($n = 14$), **4d** ($n = 15$), **4e** ($n = 16$), corresponding fatty acids were transformed to their methyl ester analogues and then to *N*-acylhydrazines (refluxing with NH_2NH_2/EtOH). The intermediates *N*-Acylhydrazines were treated with an ethanolic solution of KOH, to which CS_2 was added, to produce the corresponding carbodithioates in situ. The carbodithioates were heated to yield potassium salts of the corresponding 2-mercapto-1,3,4-oxadiazoles. The treatment of these dissolved salts with diluted $HCl_{(aq)}$ solution caused the precipitation of 5-alkyl-2,3-dihydro-1,3,4 oxadiazole-2-thiones **5a** ($n = 10$), **5b** ($n = 12$), **5c** ($n = 14$), **5d** ($n = 15$), **5e** ($n = 16$) in fairly good yields (Scheme 2).[11–15] Scheme 3 summarizes the synthetic pathway for the preparation of polyether functionalized bis-sulfanyl-2,3-dihydro-1,3,4-oxadiazoles **6a** ($n = 10$), **6b** ($n = 12$), **6c** ($n = 14$), **6d** ($n = 15$), **6e** ($n = 16$). Two equivalents of thiones **5a** ($n = 10$), **5b** ($n = 12$), **5c** ($n = 14$), **5d** ($n = 15$), **5e** ($n = 16$), and 1 equivalent of **(3)** were heated gently in the presence of 4 equivalents of K_2CO_3 with DMF as the solvent.



Scheme 3 Reagents and conditions: (i) K_2CO_3, DMF, Δ, 24 h.

Compound **6a** ($n = 10$) displayed characteristic IR bands at 3039 cm^{-1} for the aromatic $C{-}H$ stretching and at 1608 cm^{-1} for the $-C{=}N$ stretching in the 1,3,4-oxadiazole ring. The ^1H NMR spectrum of **6a** ($n = 10$) showed characteristic peaks at δ 4.39 ppm as a singlet for the $ArCH_2S-$ protons, a triplet at δ 4.10 ppm for the methylene protons next to the



Scheme 4 Reagents and conditions: (i) K_2CO_3, DMF, Δ; (ii) NH_2NH_2, MeOH, Δ; (iii) 1. CS_2, KOH, EtOH, reflux, 2. $HCl_{(aq)}$, 0°C–r.t.

aromatic ring (*−OCH₂CH₂OAr*) and a triplet at δ 2.79 ppm for the methylene protons next to the heterocyclic ring (*hetCH₂CH₂−*). The ^{13}C NMR spectra also confirm the structure of oxadiazole **6a** ($n = 10$) with several characteristic peaks at δ 168.1 ppm and δ 163.7 ppm related to the imine C atoms in the 1,3,4-oxadiazole ring. The multi-step synthetic route for the synthesis of 5-*Ph*-1,3,4-oxadiazol-2-yl- substituted 1,3,4-oxadiazole-2-thione **(9)** is shown in Scheme 4.

The starting 5-Phenyl-1,3,4-oxadiazole-2(3*H*)-thione was reacted with methyl-11-bromoundecanoate in the presence of a base and DMF to give the intermediate **(7)**. The obtained intermediate **(7)** was converted to *N*-acylhydrazine **(8)**. Compound **(8)** was treated with an ethanolic solution of KOH, to which CS_2 was added to produce the corresponding carbodithioate in situ. The carbodithioate was heated to produce the potassium salt of the corresponding 2-mercapto-1,3,4-oxadiazole. The treatment of this dissolved salt with a cooled $HCl_{(aq)}$ solution resulted in the precipitation of the final product **(9)**.

The IR spectrum of intermediate **(7)** displayed characteristic bands at 3063 cm^{-1} and at 1737 cm^{-1} for the aromatic *C−H* stretching and carbonyl group, respectively. In the ^1H NMR spectrum of **(7)**, two peaks were observed at δ 3.67 ppm as a singlet for the *OCH₃* protons and at δ 3.30 ppm as a triplet for the *hetSCH₂−* protons. The IR spectrum of **(8)** showed bands at 3316 cm^{-1}, 3195 cm^{-1}, 1638 cm^{-1}, and 1603 cm^{-1} for the *−NH₂*, *−NH−*, *C=O* and *C=N* groups, respectively. The ^1H NMR spectrum of **(8)** showed characteristic peaks at δ 6.84 ppm as a singlet for the *–NHNH₂* proton and at δ 3.90 ppm as a singlet for the two protons of the *−NHNH₂* group.

It was found that only the thione tautomer of compound **(9)** was obtained as product (Figure 1). For instance, in the IR spectrum of **(9)**, the band related to the thiol *–SH* stretching at ∼(2550–2600) cm^{-1} was not observed. The synthetic route for the formations of compounds **(10)** and **(12)** is shown in Scheme 5. The corresponding intermediates **(9)** and **(11)**[20] were reacted with bis-benzyl chloride **(3)** as a starting compound with base in DMF. Intermediate **(11)** was prepared as indicated in Scheme 6. Target compounds **(10)**

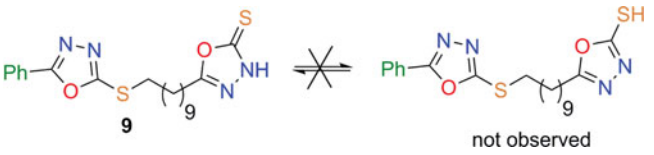
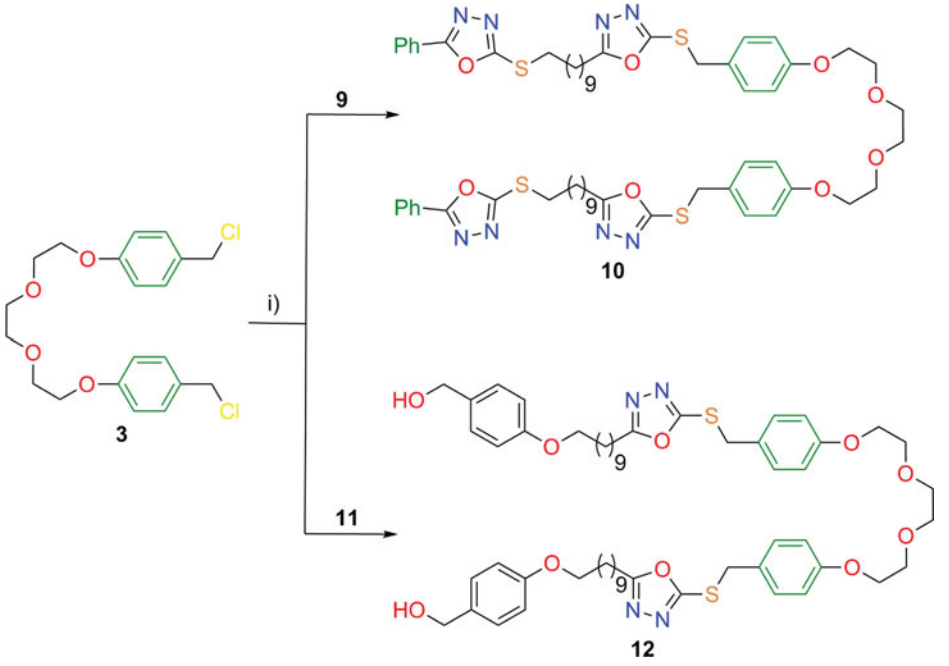


Figure 1 Thione-thiol tautomerism in compound **(9)**.

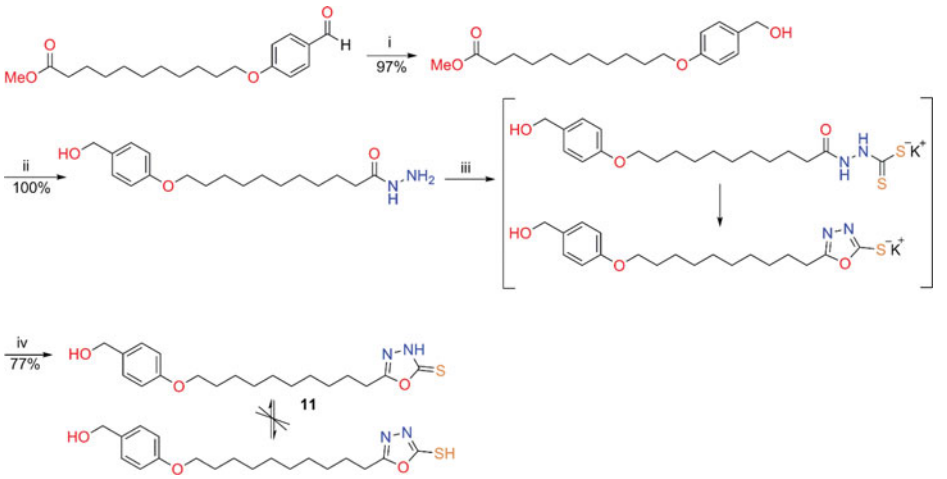
and **(12)** were obtained in 85% yields. Detailed spectral analyses of these compounds are given in the experimental section of this article.

Corrosion Test

The results obtained from the corrosion tests in mineral oil are given in Table 1. As described previously, the tests were performed at longer time periods than the 24 h required by the standard method.[21] As shown in Table 1, all of the synthesized organic compounds exhibited good inhibition efficiencies in the oil-water medium. We treated the metals for 50 h in this two-phase system containing one of the compounds synthesized in this study, but we could not observe any rust spot as evidence of corrosion. On the other hand, corrosion rust spots were observed on the metal during the first 2 h for the control sample that was subjected to the inhibitor-free mineral oil medium. The mineral oil alone was not corrosive prior to the test, as found in Control test 2 (Table 1).



Scheme 5 Reagents and conditions: (i) K_2CO_3, DMF, Δ.



Scheme 6 Synthesis of compound (11): (i) $NaBH_4$, THF/MeOH, 0°C–r.t., 1 h, (ii) NH_2NH_2, EtOH, Δ, 24 h, (iii) KOH, CS_2, EtOH, rx, 24 h, (iv) HCl(aq), 0°C.

Contact Angle Measurements

The chemical composition and the surface wettability of the metal surface change after the adsorption of inhibitor molecules. The hydrophilicity or hydrophobicity of the metal surface can be determined indirectly by water contact angle (WCA) measurements. The contact angle values for the metal surfaces (A, B, and C surfaces) are given in Table 2. The A surface refers to an untreated metal, the B surface refers to a metal without inhibitor **6d** ($n = 15$), and the C surface refers to a metal with inhibitor **6d** ($n = 15$). As indicated in the table, the concentration of **6d** ($n = 15$) was 0.05% (w/v). The contact angle values for the surfaces were an average of 10 measurements. The photographs taken from the contact angle measurements are given in Figure 2.

Table 1 Corrosion inhibition results obtained for compounds tested in a mineral oil medium with 0.05% (w/v) inhibitor at 60°C

Organic compounds	Test time in hours[a]	Results
Control 1	50	Visible yellowish or brownish corrosion rust spots on the metal surface were observed. After cleaning the metal surface with paper tissue, cavities was seen under these spots which was an evidence of pitting corrosion
Control 2	50	No visible rust spot observed
6a ($n = 10$)		
6b ($n = 12$)		
6c ($n = 14$)	50	No visible rust spot observed
6d ($n = 15$)		
6e ($n = 16$)		

[a]The time selection was random, in the relevant standard test offered time period is 24 h.

Table 2 Water contact angle values of the metal strip measured after the corrosion test in the mineral oil-water emulsion system

	Water Contact Angle (WCA) averages[a] [°]		
Surface	Metal surface before test (bare metal) A	Metal surface after test (without inhibitor) B	Metal surface after test (with inhibitor **6d**)[b] C
Metal strip	57.33 ± 0.48	94.19 ± 0.64	94.19 ± 0.64

[a]Average of the 10 meaurements.
[b]0.05% (w/v) concentration of the test compound **6d**.

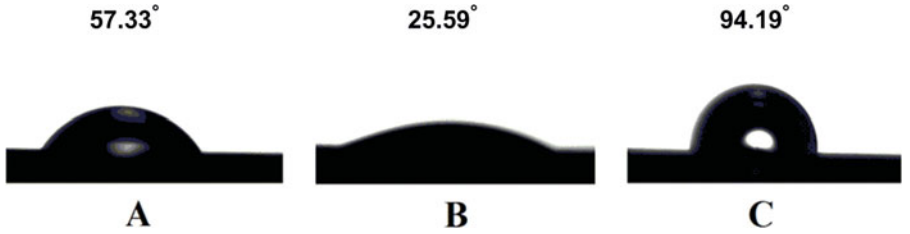


Figure 2 Images of water in-oil contact angle measurements of the metal surfaces: **A**, prior the test without any treatment: **B**, after the test without inhibitor: **C**, after the test with inhibitor **6d** ($n = 15$).

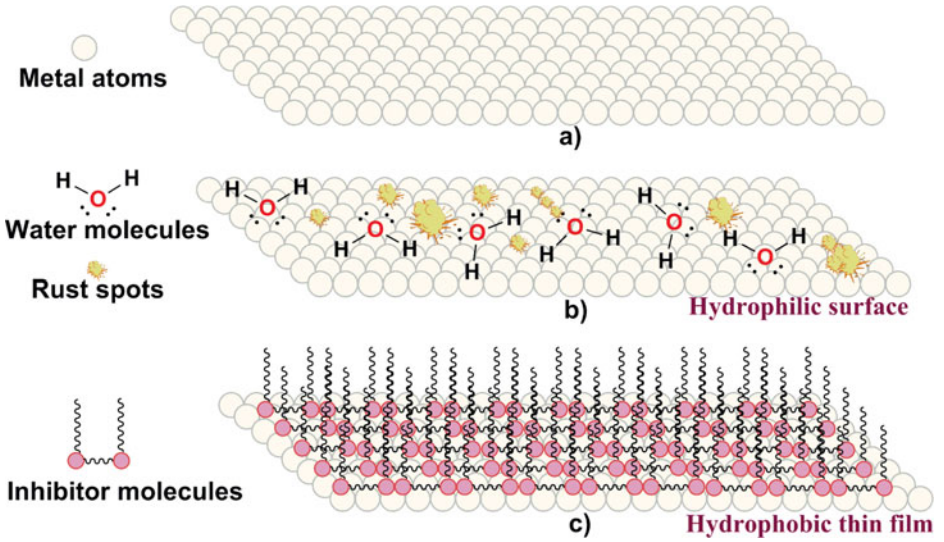


Figure 3 Representation of the metal surface; **(a)** prior the test, **(b)** during the test without inhibitor, **(c)** during the test with inhibitor.

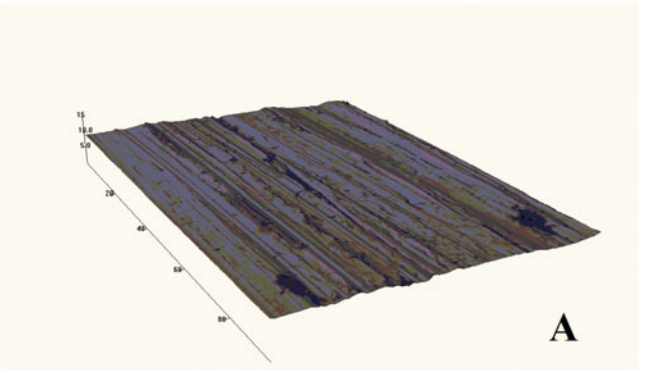


Figure 4a 3D optical profilometer image of the metal surface prior the test and without any treatment.

As shown in Table 2, the average WCA values for metal surfaces A, B, and C are 57.33°, 25.59°, and 94.19°, respectively. A comparison between metal surfaces A and C show that the inhibitor molecule increases the hydrophobic character of the surface. After the adsorption of **6d** ($n = 15$) via the polar part of the molecule, the hydrophobic parts of the molecule were oriented toward the water in the oil phase system. As a result of this orientation, a hydrophobic interface was created, causing an increase in the WCA. Therefore, the treatment with the inhibitor decreases the wettability of the metal surface. By comparing the WCA of metal surface B and metal surface A, it is observed that the lack of inhibitor **6d** ($n = 15$) causes a decrease in the hydrophobicity of the surface due to the water present in the oil. In summary, the contact angle of 57.33° was measured for samples without any treatment, indicating that the wettability of the surface of the metal strip is partially hydrophilic. With no inhibitor added in the corrosive medium, the hydrophilic character of the surface was increased (25.59°). The contact angle increases up to 94.19° after the addition of the inhibitor, making the metal surface hydrophobic. The increase in inhibitor causes the inhibitor molecules adsorbed via the heterocyclic moiety on the steel surface to form a thin oil film (Figure 3).

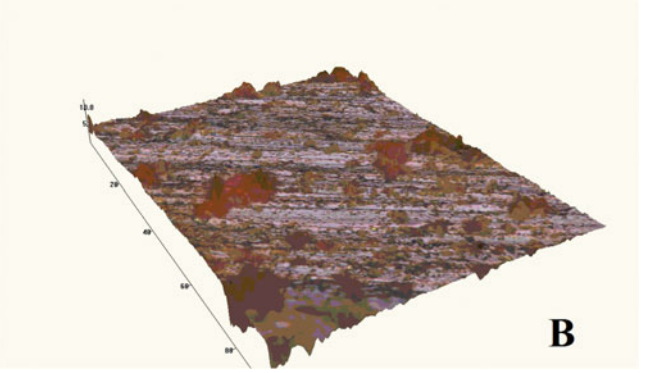


Figure 4b 3D optical profilometer image of the metal surface after the test without inhibitor.

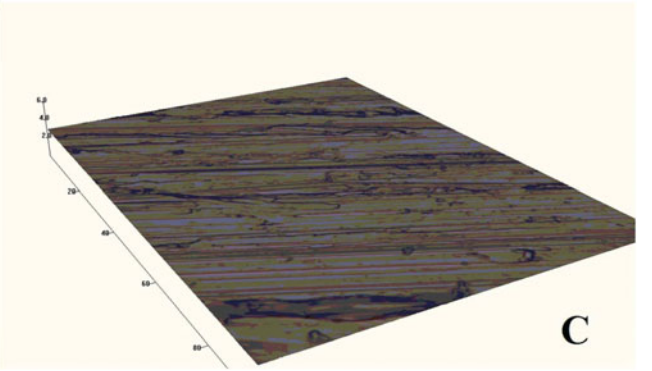


Figure 4c 3D optical profilometer image of the metal surface after the test with inhibitor **6d** ($n = 15$).

Optical Profilometer

The 3D optical profilometer images of the metal surfaces are given in Figures 4a, 4b, and 4c. The photos were taken from a 100 × magnified surface. As shown in Figure 4b, the treatment of the metal strip in the mineral oil-water medium without inhibitor leads to corrosive damages to the metal surface. Figure 4c demonstrates that the treatment of the metal strip with inhibitor prevents surface corrosion.

CONCLUSION

Consequently, in this study, we have synthesized a series of symmetric long alkyl-chained sulfanyl 1,3,4-oxadiazoles bearing a polyether head group for the first time. The heterocyclic rings in the synthesized compounds are free of hydrogen atoms, giving them high thermal stability. In addition, surface characterization studies were performed. Contact angle measurements and optical profilometer studies showed that compounds **6a** ($n = 10$), **6b** ($n = 12$), **6c** ($n = 14$), **6d** ($n = 15$), **6e** ($n = 16$), are good corrosion inhibitors in mineral oil-water system which is described in this study. The biological activities of these compounds and their applications for other industrial purposes can be explored.

EXPERIMENTAL

All reagents and solvents were purchased from either Merck or Sigma-Aldrich and used without further purification. Thin layer chromatography (TLC) was performed using silica gel (60 F_{254}, Merck, Darmstadt, Germany) plates. Melting points were recorded using a BÜCHI melting point B-540 (BUCHI Labortechnik AG in Flawil, Switzerland) apparatus. IR spectra were obtained using a Nicolet FT – IR 6700 spectrometer (Thermo Fisher Scientific Inc, Waltham, MA, USA). NMR spectra were recorded using a Varian mercury plus spectrometer (400 MHz) (Varian Inc., California, USA) in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are reported in ppm, and J values are reported in Hertz. The elemental analyses were performed on a EuroEA 3000 CHNS analyzer. The Supplemental Materials contains sample ^{1}H and ^{13}C NMR spectra of products 2, 3, 5a, 6a, 7, 8, 9, 10, 12 (Figures S1–S 18).

General Synthetic Procedures

Heptadecanehydrazide 4d (n = 15). Methyl heptadecanoate (3.2 g, 11.2 mmol) and NH_2NH_2 (1 mL, 100%) were used for the synthesis. Yield 3 g (94%); mp 115–117°C. IR (KBr): 3321, 3290, 1631. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (s, 1H, $-N\underline{H}NH_2$), 3.87 (s, 2H, $-NHN\underline{H}_2$), 2.14 (t, $J = 7.2$ Hz, 2H, $-C{=}OC\underline{H}_2CH_2-$), 1.63 (quin, $J = 7.2$ Hz, 2H, $-C{=}OCH_2C\underline{H}_2CH_2-$), 1.32–1.23 (m, 26H, $-C\underline{H}_2-$), 0.87 (t, $J = 6.8$ Hz, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 34.6, 31.9, 29.7 (2C), 29.6 (2C), 29.5, 29.4, 29.3 (2C), 25.5, 22.7, 14.1. Anal calc for $C_{17}H_{36}N_2O$ (284.49): C 71.77, H 12.76, N 9.85. Found: C 71.93, H 12.66, N 9.52.

General method for the synthesis of 5-alkyl-2,3-dihydro-1,3,4-oxadiazole-2-thiones 5a ($n = 10$), **5b** ($n = 12$), **5c** ($n = 14$), **5d** ($n = 15$), **5e** ($n = 16$)[11–15] Potassium hydroxide (1.5 equivalents) was dissolved in a minimum amount of water and EtOH (50 mL) was added. Hydrazide **4a** ($n = 10$), **4b** ($n = 12$), **4c** ($n = 14$), **4d** ($n = 15$), **4e** ($n = 16$) (1 equivalent) was added dropwise to the above basic solution. After the formation of a clear solution, CS_2 (1.5 equivalents) was added dropwise and refluxed for 24 h. The solvent was evaporated under vacuum, and a large quantity of ice-cooled water was added. Afterwards, the solution was acidified with diluted $HCl_{(aq)}$. The observed solid was filtered under vacuum and dried at room temperature for 24 h. It was crystallized from EtOH/H_2O as a white crystalline solid.

5-Undecyl-2,3-dihydro-1,3,4-oxadiazole-2-thione 5a (*n* = 10)

Hydrazide **4a** ($n = 10$) (4.5 g, 21 mmol), KOH (1.77 g, 31.5 mmol) and CS_2 (1.9 mL, 31.5 mmol) were used for the synthesis. Yield 4.9 g (91%); mp 71–72°C. IR (KBr): 3205, 1620, 1173, 1057. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.97 (s, 1H, $-N\underline{H}$), 2.69 (t, $J = 7.6$ Hz, 2H, $-C\underline{H}_2-$het), 1.75 (quin, $J = 7.6$ Hz, 2H, $-CH_2C\underline{H}_2CH_2-$het), 1.43–1.23 (m, 16H, $-CH_2-$), 0.87 (t, $J = 6.8$ Hz, 3H, $-C\underline{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 164.9, 31.9, 29.5 (2C), 29.3 (2C), 29.0, 28.8, 25.7, 25.5, 22.7, 14.1. Anal calc for $C_{13}H_{24}N_2OS$ (256.41): C 60.89, H 9.43, N 10.93, S 12.51. Found: C 60.45, H 9.40, N 10.56, S 12.70.

5-Tridecyl-2,3-dihydro-1,3,4-oxadiazole-2-thione 5b (*n* = 12)

Hydrazide **4b** ($n = 12$) (1.9 g, 7.9 mmol), KOH (0.66 g, 11.9 mmol), and CS_2 (0.72 mL, 11.9 mmol) were used for the synthesis. Yield 2.23 g (100%); mp 79–80°C. IR (KBr): 3205, 1620, 1176, 1065. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.91 (s, 1H, $-N\underline{H}$), 2.69 (t, $J = 7.5$ Hz, 2H, $-C\underline{H}_2-$het), 1.73 (quin, $J = 7.2$ Hz, 2H, $-CH_2C\underline{H}_2CH_2-$het), 1.43–1.21 (m, 20H, $-CH_2-$), 0.87 (t, $J = 6.8$ Hz, 3H, $-C\underline{H}_3$). ^{13}C NMR (100, MHz, $CDCl_3$) δ 178.5, 164.9, 31.9, 29.6 (3C), 29.5, 29.3, 29.0, 28.8, 25.7, 25.5, 22.7, 14.1. Anal calc for $C_{15}H_{28}N_2OS$ (284.46): C 63.33, H 9.92, N 9.85, S 11.27. Found: C 63.20, H 9.87, N 9.63, S 11.59.

5-Pentadecyl-2,3-dihydro-1,3,4-oxadiazole-2-thione 5c (*n* = 14)

Hydrazide **4c** ($n = 14$) (0.91 g, 3.36 mmol), KOH (0.28 g, 5.04 mmol), and CS_2 (0.3 mL, 5.04 mmol) were used for the synthesis. Yield 1 g (95%); mp 83–84°C. IR (KBr): 3205, 1620, 1176, 1068. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.93 (s, 1H, $-N\underline{H}$), 2.69 (t, J 7.6 Hz, 2H, $-C\underline{H}_2-$het), 1.74 (quin, $J = 7.5$ Hz, 2H, $-CH_2C\underline{H}_2CH_2-$het), 1.43–1.22

(m, 24H, $-CH_2-$), 0.87 (t, $J = 6.4$ Hz, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 164.9, 31.9, 29.5 (2C), 29.3 (2C), 29.0, 28.8, 25.7, 25.5, 22.7, 14.1. Anal calc for $C_{17}H_{32}N_2OS$ (312.52): C 65.34, H 10.32, N 8.96, S 10.26. Found: C 65.15, H 10.09, N 8.49, S 10.28.

5-Hexadecyl-2,3-dihydro-1,3,4-oxadiazole-2-thione 5d ($n = 15$)

Hydrazide **4d** ($n = 15$) (2.9 g, 10.2 mmol), KOH (0.86 g, 15.3 mmol), and CS_2 (0.92 mL, 15.3 mmol) were used for the synthesis. Yield 3 g (87%); mp 89–90°C. IR (KBr): 3205, 1624, 1165, 1072. ^1H NMR (400 MHz, $CDCl_3$) δ 10.96 (s, 1H, $-NH$), 2.69 (t, $J = 7.6$ Hz, 2H, $-CH_2-$het), 1.74 (quin, $J = 7.4$ Hz, 2H, $-CH_2CH_2CH_2-$het), 1.43–1.18 (m, 26H, $-CH_2-$), 0.87 (t, $J = 6.8$ Hz, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 164.9, 31.9, 29.7 (3C), 29.6, 29.5, 29.4, 29.3, 29.0, 28.8, 25.7, 25.5, 22.7, 14.1. Anal calc for $C_{18}H_{34}N_2OS$ (326.54): C 66.21, H 10.49, N 8.58, S 9.82. Found: C 66.26, H 10.55, N 8.03, S 9.32.

5-Heptadecyl-2,3-dihydro-1,3,4-oxadiazole-2-thione 5e ($n = 16$)

Hydrazide **4e** ($n = 16$) (0.5 g, 1.47 mmol), KOH (0.12 g, 2.21 mmol), and CS_2 (0.13 mL, 2.21 mmol) were used for the synthesis. Yield 0.47 g (82%); mp 90 – 91°C. IR (KBr): 3205, 1612, 1165, 1053. ^1H NMR (400 MHz, $CDCl_3$) δ 10.93 (s, 1H, $-NH$), 2.69 (t, $J = 7.5$ Hz, 2H, $-CH_2-$het), 1.75 (quin, $J = 7.4$ Hz, 2H, $-CH_2CH_2CH_2-$het), 1.43–1.22 (m, 28H, $-CH_2-$), 0.87 (t, $J = 6.8$ Hz, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 164.9, 31.9, 29.7 (2C), 29.6, 29.5, 29.4, 29.3, 29.0, 28.8, 25.7, 25.5, 22.7, 14.1. Anal calc for $C_{19}H_{36}N_2OS$ (340.57): C 67.01, H 10.65, N 8.23, S 9.42. Found: C 66.90, H 10.66, N 8.04, S 9.64.

General method for the synthesis of semi-crown ether functionalized bis-sulfanyl-2,3-dihydro-1,3,4-oxadiazoles 6a ($n = 10$), **6b** ($n = 12$), **6c** ($n = 14$), **6d** ($n = 15$), **6e** ($n = 16$).

Intermediates **5a** ($n = 10$), **5b** ($n = 12$), **5c** ($n = 14$), **5d** ($n = 15$), **5e** ($n = 16$) (2 equivalents) were dissolved in DMF (20 mL), and then K_2CO_3 (4 equivalents) was added. After stirring for 10 min at room temperature, bis-benzyl chloride **(3)** (1 equivalent) was added and the reaction was heated for 24 h. The reaction mixture was cooled, and ice-cooled water was added. The precipitated product was filtered under vacuum and dried at room temperature. The products were crystallized from suitable solvents, which are given below for each individual compound.

2-Undecyl-5-({[4-(2-{2-[2-(4-{[(5-undecyl-1,3,4-oxadiazol-2-yl)sulfanyl]methyl}phenoxy)ethoxy]ethoxy}ethoxy)phenyl]methyl}sulfanyl)-1,3,4-oxadiazole 6a ($n = 10$)

Intermediate **5a** ($n = 10$) (0.87 g, 3.39 mmol), bis-benzyl chloride **(3)** (0.68 g, 1.70 mmol), K_2CO_3 (0.94 g, 6.80 mmol), and DMF (15 mL) were used for the synthesis. The product was crystallized from acetone/petroleum ether as shiny white crystals. Yield 1.2 g (85%); mp 95–96°C. IR (KBr): 3039, 1608, 1242. ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 4H, Ar), 6.87–6.83 (m, 4H, Ar), 4.39 (s, 4H, $2ArCH_2S$), 4.10 (t, $J = 4.8$ Hz, 4H, $2\,OCH_2CH_2OAr$), 3.85 (t, $J = 4.8$ Hz, 4H, $2OCH_2CH_2OAr$), 3.74 (s, 4H, OCH_2CH_2O), 2.79 (t, $J = 7.6$ Hz, 4H, $2hetCH_2CH_2-$), 1.74 (quin, $J = 7.6$ Hz, 4H, $2hetCH_2CH_2CH_2-$),

1.42–1.22 (m, 32H, $-CH_2-$), 0.87 (t, J = 6.4 Hz, 6H, $2-CH_3$), ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 163.7, 158.6, 130.3, 127.7, 114.8, 70.9, 69.7, 67.4, 36.3, 31.9, 29.6, 29.4, 29.1, 29.0, 26.4, 25.4, 22.4, 14.1. Anal calc for $C_{46}H_{70}N_4O_6S_2$ (839.21): C 65.84, H 8.41, N 6.68, S 7.64. Found: C 66.79, H 8.35, N 6.22, S 7.31.

2-Tridecyl-5-({[4-(2-{2-[2-(4-{[(5-tridecyl-1,3,4-oxadiazol-2-yl)sulfanyl]methyl}phenoxy)ethoxy]ethoxy}ethoxy)phenyl]methyl}sulfanyl)-1,3,4-oxadiazole 6b (n = 12)

Intermediate **5b** (n = 12) (0.67 g, 2.36 mmol), bis-benzyl chloride **(3)** (0.47 g, 1.18 mmol), K_2CO_3 (0.65 g, 4.72 mmol), and DMF (15 mL) were used for the synthesis. The product was crystallized from acetone/petroleum ether as white crystals. Yield 1.01 g (96%); mp 100–101°C. IR (KBr): 3039, 1612, 1242. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.30 (m, 4H, Ar), 6.86–6.84 (m, 4H, Ar), 4.39 (s, 4H, $2ArC\underline{H}_2S$), 4.10 (t, J = 4.4 Hz, 4H, $2\ OCH_2C\underline{H}_2OAr$), 3.84 (t, J = 4.4 Hz, 4H, $2OC\underline{H}_2CH_2OAr$), 3.73 (s, 4H, $OC\underline{H}_2C\underline{H}_2O$), 2.79 (t, J = 7.6 Hz, 4H, $2hetC\underline{H}_2CH_2-$), 1.74 (quin, J = 7.5 Hz, 4H, $2hetCH_2C\underline{H}_2CH_2-$), 1.42–1.22 (m, 40H, $-CH_2-$), 0.87 (t, J = 6.7 Hz, 6H, $2-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 163.7, 158.6, 130.3, 127.7, 114.8, 70.9, 69.7, 67.4, 36.4, 31.9, 29.7, 29.6 (2C), 29.4, 29.3, 29.1, 29.0, 26.4, 25.4, 22.7, 14.1. Anal calc for $C_{50}H_{78}N_4O_6S_2$ (895.32): C 67.08, H 8.78, N 6.26, S 7.16. Found: C 67.32, H 8.20, N 6.71, S 6.99.

2-Pentadecyl-5-({[4-(2-{2-[2-(4-{[(5-pentadecyl-1,3,4-oxadiazol-2-yl)sulfanyl]methyl}phenoxy)ethoxy]ethoxy}ethoxy)phenyl]methyl}sulfanyl)-1,3,4-oxadiazole 6c (n = 14)

Intermediate **5c** (n = 14) (0.47 g, 1.50 mmol), bis-benzyl chloride **(3)** (0.30 g, 0.75 mmol), K_2CO_3 (0.41 g, 2.97 mmol), and DMF (15 mL) were used for the synthesis. The product was crystallized from AcOEt/petroleum ether as white crystals. Yield 0.7 g (98%); mp 103–104°C. IR (KBr): 3039, 1612, 1242. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.30 (m, 4H, Ar), 6.87–6.84 (m, 4H, Ar), 4.39 (s, 4H, $2ArC\underline{H}_2S$), 4.10 (t, J = 4.4 Hz, 4H, $2\ OCH_2C\underline{H}_2OAr$), 3.85 (t, J = 4.8 Hz, 4H, $2OC\underline{H}_2CH_2OAr$), 3.74 (s, 4H, $OC\underline{H}_2C\underline{H}_2O$), 2.79 (t, J = 7.6 Hz, 4H, $2hetC\underline{H}_2CH_2-$), 1.74 (quin, J = 7.6 Hz, 4H, $2hetCH_2C\underline{H}_2CH_2-$), 1.42–1.22 (m, 48H, $-CH_2-$), 0.87 (t, J = 6.4 Hz, 6H, $2-CH_3$). ^{13}C NMR (400 MHz, $CDCl_3$) δ 168.1, 163.7, 158.6, 130.3, 127.7, 114.8, 70.9, 69.7, 67.4, 36.4, 31.9, 29.7 (3C), 29.6 (2C), 29.4, 29.3, 29.1, 29.0, 26.4, 25.4, 22.7, 14.1. Anal calc for $C_{54}H_{86}N_4O_6S_2$ (951.42): C 68.17, H 9.11, N 5.89, S 6.74. Found: C 68.32, H 9.04, N 5.71, S 6.99.

2-Hexadecyl-5-({[4-(2-{2-[2-(4-{[(5-hexadecyl-1,3,4-oxadiazol-2-yl)sulfanyl]methyl}phenoxy)ethoxy]ethoxy}ethoxy)phenyl]methyl}sulfanyl)-1,3,4-oxadiazole 6d (n = 15)

Intermediate **5d** (n = 15) (0.51 g, 1.56 mmol), bis-benzyl chloride **(3)** (0.31 g, 0.78 mmol), K_2CO_3 (0.43 g, 3.12 mmol), and DMF (15 mL) were used for the synthesis. The product was crystallized from AcOEt/petroleum ether as white crystals. Yield 0.75 g (100%); mp 104 – 105°C. IR (KBr): 3039, 1608, 1242. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.30 (m, 4H, Ar), 6.87 – 6.84 (m, 4H, Ar), 4.39 (s, 4H, $2ArC\underline{H}_2S$), 4.10 (t, J = 4.8 Hz, 4H, $2\ OCH_2C\underline{H}_2OAr$), 3.85 (t, J = 4.4 Hz, 4H, $2OC\underline{H}_2CH_2OAr$), 3.74 (s, 4H, $OC\underline{H}_2C\underline{H}_2O$), 2.79 (t, J = 7.6 Hz, 4H, $2hetC\underline{H}_2CH_2-$), 1.74 (quin, J = 7.5 Hz, 4H, $2hetCH_2C\underline{H}_2CH_2-$), 1.40–1.23 (m, 52H, $-CH_2-$), 0.87 (t, J = 6.7 Hz, 6H, $2-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 163.7, 158.6, 130.3, 127.7, 114.8, 70.9, 69.7, 67.4, 36.4, 31.9, 29.7(3C), 29.6 (2C), 29.4, 29.3, 29.1, 29.0, 26.4, 25.4, 22.7, 14.1. Anal calc for $C_{56}H_{90}N_4O_6S_2$ (979.48): C 68.27, H 9.26, N 5.72, S 6.55. Found: C 68.02, H 9.24, N 5.71, S 6.86.

2-Heptadecyl-5-({[4-(2-{2-[2-(4-{[(5-heptadecyl-1,3,4-oxadiazol-2-yl)sulfanyl]methyl}phenoxy)ethoxy]ethoxy}ethoxy)phenyl]methyl}sulfanyl)-1,3,4-oxadiazole 6e ($n = 16$)

Intermediate **5e** ($n = 16$) (0.41 g, 1.20 mmol), bis-benzyl chloride **(3)** (0.24 g, 0.60 mmol), K_2CO_3 (0.33 g, 2.40 mmol), and DMF (15 mL) were used for the synthesis. The product was crystallized from AcOEt/petroleum ether as white crystals. Yield 0.52 g (86%); mp 106–107°C. IR (KBr): 3039, 1612, 1242. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.29 (m, 4H, Ar), 6.87–6.83 (m, 4H, Ar), 4.39 (s, 4H, 2ArC$\underline{H}_2$S), 4.10 (t, J = 4.4 Hz, 4H, 2 OCH$_2$C$\underline{H}_2$OAr), 3.85 (t, J = 4.8 Hz, 4H, 2OC$\underline{H}_2$CH$_2$OAr), 3.74 (s, 4H, OC$\underline{H}_2$C$\underline{H}_2$O), 2.79 (t, J = 7.6 Hz, 4H, 2hetC$\underline{H}_2$CH$_2-$), 1.73 (quin, J = 7.4 Hz, 4H, 2hetCH$_2$C$\underline{H}_2$CH$_2-$), 1.41–1.20 (m, 56H, $-$CH$_2-$), 0.88 (t, J = 6.8 Hz, 6H, 2$-$CH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 163.7, 158.6, 130.3, 127.7, 114.8, 70.9, 69.7, 67.4, 36.4, 31.9, 29.7 (2C), 29.6 (2C), 29.4 (2C), 29.1, 29.0, 26.4, 25.4, 22.7, 14.1. Anal calc for $C_{58}H_{94}N_4O_6S_2$ (1007.53): C 69.14, H 9.40, N 5.56, S 6.37. Found: C 69.24, H 9.24, N 5.71, S 6.76.

Synthesis of methyl-11-[(5-phenyl-1,3,4-oxadiazol-2-yl)sulfanyl]undecanoate (7). To a solution of 5-phenyl-1,3,4-oxadiazole-2(3*H*)-thione (2.68 g, 15.04 mmol) in DMF (20 mL), methyl-11-bromoundecanoate (4.2 g, 15.04 mmol) and K_2CO_3 (4 g, 30.39 mmol) were added. The contents of the flask were stirred and heated for 24 h. Thereafter, the reaction mixture was cooled and cold water was added. The precipitated solid product was filtered, washed with water and dried at room temperature for 24 h. It was crystallized from hexane/AcOEt as a cream-colored solid. Yield 4.4 g (78%); mp 62–63°C. IR (KBr): 3063, 1737, 1555. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–8.00 (m, 2H, Ar), 7.53–7.47 (m, 2H, Ar), 3.67 (s, 3H, $-$OCH$_3$), 3.30 (t, J = 7.6 Hz, 2H, hetSC$\underline{H}_2$CH$_2-$), 2.30 (t, J = 7.2 Hz, 2H, CH$_3$OC=OC$\underline{H}_2$CH$_2-$), 1.84 (quin, J = 7.2 Hz, 2H, hetSCH$_2$C$\underline{H}_2$CH$_2-$), 1.46 (quin, J = 7.6 Hz, 2H, CH$_3$OC=OC$\underline{H}_2$CH$_2$CH$_2-$), 1.37–1.25 (m, 12H, $-$CH$_2-$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 165.6, 164.6, 131.6, 129.0, 126.6, 123.7, 51.5, 34.1, 32.6, 29.4, 29.3, 29.2 (2C), 29.1, 29.0, 28.6, 24.9. Anal calc for $C_{20}H_{28}N_2O_3S$ (376.51): C 63.80, H 7.50, N 7.44, S 8.52. Found: C 63.80, H 7.67, N 7.23, S 8.05.

Synthesis of 11-[(5-phenyl-1,3,4-oxadiazol-2-yl)sulfanyl]undecanehydrazide (8). To a solution of ester **(7)** (4.2 g, 11.2 mmol) in MeOH (30 mL), NH_2NH_2 (2.5 mL, 100%) was added, and the resulting mixture was heated for 24 h. Ethanol was removed using a rotary evaporator. Over the residue, cold water was added and the observed solid was filtered under vacuum, dried at room temperature and crystallized from AcOEt/hexane/MeOH as shiny white crystals. Yield 3.5 g (83%); mp 89–90°C. IR (KBr): 3316, 3195, 3058, 1638, 1603. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–8.00 (m, 2H, Ar); 7.55–7.47 (m, 2H, Ar), 6.84 (s, 1H, $-$N$\underline{H}$NH$_2$), 3.90 (s, 2H, $-$NHN$\underline{H}_2$), 3.30 (t, J = 7.6 Hz, 2H, hetSC$\underline{H}_2$CH$_2-$), 2.15 (t, J = 7.6 Hz, 2H, $-$C=OC$\underline{H}_2$CH$_2-$), 1.84 (quin, J = 7.2 Hz, 2H, hetSCH$_2$C$\underline{H}_2$CH$_2-$), 1.63 (t, J = 7.2 Hz, 2H, hetSCH$_2$CH$_2$C$\underline{H}_2$CH$_2-$), 1.46 (quin, J = 7.2Hz, 2H, $-$C=OCH$_2$C$\underline{H}_2$CH$_2-$), 1.37–1.26 (m, 10H, $-$CH$_2-$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 165.6, 164.6, 131.6, 129.0, 126.6, 123.7, 34.5, 32.6, 29.2 (4C), 28.9, 28.5, 25.5. Anal calc for $C_{19}H_{28}N_4O_2S$ (376.52): C 60.61, H 7.50, N 14.88, S 8.52. Found: C 60.27, H 7.55, N 14.51, S 8.19.

Synthesis of 5-{10-[(5-phenyl-1,3,4-oxadiazol-2-yl)sulfanyl]decyl}-2,3-dihydro-1,3,4-oxadiazole-2-thione (9). Into a flask containing KOH (0.5 g,

8.91 mmol) dissolved in a minimum amount of water, EtOH (30 mL) was added. Thereafter, hydrazide **(8)** (2.2 g, 5.84 mmol) was added dropwise to the above basic solution. After the formation of a clear solution, CS_2 (1 mL) was dropped and refluxed for 24 h. The solvent was evaporated under vacuum, and a large amount of ice-cooled water was added. Afterwards, the solution was acidified with diluted $HCl_{(aq)}$. The observed solid was filtered under vacuum and dried at room temperature for 24 h. It was crystallized from AcOEt/hexane/EtOH as a white solid. Yield 1.5 g (63%); mp 129.5–131°C. IR (KBr): 3088, 1627, 1560, 1196. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.01 (m, 2H, Ar), 7.54–7.48 (m, 2H, Ar), 3.30 (t, $J = 7.6$ Hz, 2H, hetSCH_2CH_2-), 2.70 (t, $J = 7.2$ Hz, 2H, $-CH_2CH_2$het), 1.86 (quin, $J = 7.6$ Hz, 2H, het$SCH_2CH_2CH_2-$), 1.75 (t, $J = 7.2$ Hz, 2H, $-CH_2CH_2CH_2$het), 1.46 (quin, $J = 8.0$ Hz, 2H, $-CH_2CH_2CH_2CH_2$het), 1.37–1.25 (m, 10H, $-CH_2-$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.7, 165.7, 164.9, 164.6, 131.7, 129.1, 126.7, 123.4, 32.6, 29.2, 29.0, 28.7, 28.6, 28.5, 28.4 (2C), 25.6, 25.4. Anal calc for $C_{20}H_{26}N_4O_2S_2$ (418.57): C 57.39, H 6.26, N 13.39, S 15.32 Found: C 57.32, H 6.40, N 13.03, S 14.71.

Synthesis of 2-phenyl-5-({10-[5-({[4-(2-{2-[2-(4-{[(5-{10-[(5-phenyl-1,3,4-oxadiazol-2-yl)sulfanyl]decyl}-1,3,4-oxadiazol-2-yl)sulfanyl]methyl}phenoxy)ethoxy]ethoxy}ethoxy)phenylmethyl}sulfanyl)-1,3,4-oxadiazol-2-yl]decyl}sulfanyl)-1,3,4-oxadiazole (10). To a solution of **(9)** (1.07 g, 2.56 mmol) and K_2CO_3 (1 g, 7.24 mmol) in DMF (15 mL), bisbenzyl chloride **(3)** (0.51 g, 1.28 mmol) was added, and the mixture was heated with stirring for 24 h. The reaction mixture was cooled, and ice-cooled water was added. The product was extracted with $CHCl_3$, and the organic phase was dried over Na_2SO_4. The solvent was removed using a rotary evaporator, and the residue was crystallized from acetone/petroleum ether as a white solid. Yield 1.27 g (85%); mp 85–86°C. IR (KBr): 3059, 1612, 1261. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.99 (m, 4H, Ar), 7.54–7.46 (m, 6H, Ar), 7.33–7.29 (m, 4H, Ar), 6.87–6.83 (m, 4H, Ar), 4.39 (s, 4H, $2-ArCH_2S-$het), 4.10 (t, $J = 4.8$ Hz, 4H, $2-CH_2OAr-$), 3.84 (t, $J = 4.8$ Hz, 4H, $2-CH_2CH_2OAr-$), 3.73 (s, 4H, $-OCH_2CH_2O-$), 3.29 (t, $J = 7.6$ Hz, 4H, $2-CH_2CH_2S-$hetAr), 2.79 (t, $J = 7.6$ Hz, 4H, $2S-$hetCH_2CH_2-), 1.83 (quin, J 7.6 Hz, 4H, $2-CH_2CH_2CH_2S-$hetAr), 1.73 (quin, $J = 7.6$ Hz, 4H, $2ArCH_2S-$het$CH_2CH_2CH_2-$), 1.46 (quin, $J = 7.2$ Hz, 4H, $2ArCH_2S-$het$CH_2CH_2CH_2CH_2-$), 1.40–1.25 (m, 20H, $-CH_2-$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 165.6, 164.6, 163.7, 158.6, 131.6, 130.3, 129.0, 127.7, 126.6, 123.7, 114.8, 70.9, 69.7, 67.4, 36.3, 32.6, 29.3, 29.2, 29.0 (2C), 28.9, 28.5, 26.4, 25.4. Anal calc for $C_{60}H_{74}N_8O_8S_4$ (1163.54): C 61.94, H 6.41, N 9.63, S 11.02. Found: C 61.36, H 6.40, N 9.55, S 10.71.

Synthesis of [4-({10-[5-({[4-(2-{2-[2-(4-{[(5-{10-[4-hydroxymethyl)phenoxy]decyl}-1,3,4-oxadiazol-2- yl)sulfanyl]methyl}phenoxy)ethoxy]ethoxy}ethoxy)phenyl]methyl}sulfanyl)-1,3,4-oxadiazol-2-yl]decyl}oxy)phenyl]methanol (12). To a solution of **(11)**[20] (0.68 g, 1.87 mmol) and K_2CO_3 (0.8 g, 5.79 mmol) in DMF (15 mL), bis-benzyl chloride **(3)** (0.37 g, 0.93 mmol) was added, and the mixture was heated with stirring for 24 h. The reaction mixture was cooled, and ice-cooled water was added. The precipitated product was filtered under vacuum, dried at room temperature and crystallized from acetone/petroleum ether as a white solid. Yield 0.84 g (85%); mp 103–104°C. IR (KBr): 3340, 3062, 1612. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 8H, Ar), 6.88–6.84 (m, 8H, Ar), 4.61 (s, 4H, $2-OArCH_2OH$), 4.39 (s, 4H, $2-ArCH_2S-$het), 4.10 (t, $J = 4.8$ Hz, 4H, $2-CH_2OAr-$), 3.94 (t, $J = 6.6$ Hz, 4H, $-CH_2OArCH_2OH$), 3.84 (t, $J = 4.8$ Hz, 4H, $2-CH_2CH_2OAr$), 3.73 (s, 4H, $-OCH_2CH_2O-$), 2.78 (t, $J = 7.6$ Hz, 4H, $2S-$hetCH_2CH_2-), 1.80–1.70 (m, 4H, $2S-$het$CH_2CH_2CH_2-$), 1.44 (quin, $J = 7.2$ Hz, 4H, $2-CH_2CH_2CH_2OArCH_2OH$),

1.35–1.27 (m, 24H, $-CH_2-$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 163.7, 158.7, 158.6, 132.9, 130.3, 128.6, 127.7, 114.8, 114.5, 70.9, 69.7, 68.0, 67.4, 65.0, 36.3, 29.4, 29.3 (2C), 29.2, 29.0, 28.9, 26.4, 26.0, 25.4. Anal calc for $C_{58}H_{78}N_4O_{10}S_2$ (1055.40): C 66.01, H 7.45, N 5.31, S 6.08. Found: C 66.25, H 7.31, N 5.24, S 5.71.

Corrosion Tests

Preparation of the Test Metal and Oil Solution. The metals strips and oil solutions were prepared and used in accordance with the literature.[21] The metals had a length of 7 cm and a diameter of 1.1 cm. The elemental compositions of the metals in wt% were 0.15–0.20% C, 0.15–0.35% Pb, 0.60–0.90% Mn, and no more than 0.040% P, 0.050% S, and 0.10% Si. The metals were cleaned with a suitable solvent and dried before testing in the mineral oil medium. The oil used in this study was Spindle base oil (only produced by Izmir Refinery in Turkey) composed of 70–72% paraffin, 0% olefin, 18–20% naphthene, and 10–12% aromatic. The oil has a flash point of at least 180°C, pour point (max) of –15°C, viscosity index (min) of 95, trace amounts of sediment and water (vol%), Neut. No. TAN (mg KOH/g, max) of 0.1, and sulfur including heavy aromatic sulfurs, that are not corrosive.

Observation for Rust Spots on the Metal Strips. All tests in the mineral oil medium were performed according to the Turkish Standard method (TS) 6830 ISO 7120,[22] but the treatment periods were extended to 50 h instead of 24 h. Mineral oil (100 mL) and one of the synthesized corrosion inhibitors, **(6a–e)**, were added to the (150 mL) glass cylinder with a final concentration of 0.1% (w/v). The solution was gently heated to reach the required solubility. When the inhibitor was completely dissolved, metal strips attached to a support were immersed into open cap glass cylinders filled with the oil solution. Next, the cylinders were placed in a glycerin bath heated on a heater (Heidolph MR 3001 K, Heidolph Instruments GmbH & Co.KG, Schwabach, Germany) fitted with an electronic thermometer (Heidolph EKT 3001, Heidolph Instruments GmbH & Co.KG, Schwabach, Germany), stirred at 700 rpm and maintained at 60°C for 30 min. Distilled water (10 mL) was slowly added, and the reaction was stirred for up to 50 h at 60°C. Afterwards, the metal strips were treated as follows: the metal strips were removed, wiped carefully with paper tissue and compared with the control metal strip. Two different tests were performed as controls. Control test 1 consisted of one metal strip immersed into a stirred mineral oil–water medium and maintained at 60°C for 50 h. Control test 2 consisted of another metal strip immersed into a stirred solution of simple mineral oil and maintained at 60°C for 50 h.

Contact Angle Measurements

The contact angles of the metal strip surfaces were determined using a KSV Attention Theta (Hamburg, Germany) instrument. Prior to measuring the contact angles, the metal strips were cooled to room temperature in a vacuum desiccator after performing the inhibition test in the oil-water emulsion system. The contact angles of the surfaces were measured using the sessile drop method by dropping water onto the metal strip surface from a 10 mL syringe. Ten separate photos were taken for the different sections of the surface, and the contact angle values were measured for each drop. The measured contact angle values were the left contact angle, which is the angle from the left contact point of the droplet with the solid, and the right contact angle, which is from the right contact point. Average contact angle values were obtained from the average of the two values. The contact angle values for the surfaces were the average of 10 measurements.

Optical Profilometer Images

To characterize the surfaces of the metal strips, a Zeta–20 True Color 3D Optical Profiler (Zeta Instruments, CA, USA) was used. Metal strips, which were maintained in a vacuum desiccator after the inhibition test, were mounted onto a sample holder placed under the objective of the Optical Profiler. 3D photos of the 100 × magnified surface were captured via the operating program on the computer.

SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher's website at http://dx.doi.org/10.1080/10426507.2014.999067

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