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Long-Chain Alkylthia-Benzimidazoles as Corrosion Inhibitors for Carbon Steel in H₂SO₄ Solution

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LONG-CHAIN ALKYLTHIA-BENZIMIDAZOLES AS CORROSION INHIBITORS FOR CARBON STEEL IN $\rm H_2SO_4$ SOLUTION

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GRAPHICAL ABSTRACT



Abstract A series of long-chain N-arylundecanamides containing benzimidazole thioethers (2a–e) were synthesized and characterized by FT IR, ¹H NMR, and elemental analysis. The corrosion inhibitory properties of these compounds on cold rolled low carbon steel metal coupons were investigated by weight loss measurements in acidic media. Surface characterization studies of the metal coupons used were performed by contact angle measurements using the sessile-drop method. In addition, the 3D image of the metal surface was measured using an optical profilometer. The results obtained from these analyses showed that almost all of the tested compounds between 25–150-ppm concentrations in acidic media are good to excellent corrosion inhibitors with the values of percentage inhibition efficiency (η) = 77–99%.

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Keywords Synthesis; long-chain alkylthia-benzimidazoles; corrosion inhibitors; acidic media

INTRODUCTION

Corrosion prevention of metallic materials is one of the tedious tasks for industrial chemists.¹ Certain heterocyclic compounds named as corrosion inhibitors are widely used for this purpose.^{2–6} In general, inhibitors are organic compounds with certain functional

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groups or heterocyclic moieties. These compounds are adsorbed on the metal surface to form a protective layer against the corrosive medium. In the corrosion literature, there are many papers related to inhibitors containing the benzimidazole ring.^{7–14} Compounds, including this heterocyclic system, are suitable corrosion inhibitors for various metals in different aggressive mediums. (1*H*-Benzo[*d*]imidazol-2-yl)methanethiol, also known as 2-mercaptomethyl benzimidazole, has an aromatic π electrons cloud, five-membered diazole ring, and thiol group that play important roles in corrosion inhibition.

In order to use organic compounds as corrosion inhibitors, some points must be considered. For instance, these compounds should be easily prepared and must be chemically stable under the conditions of use. In addition, maximum protection should be obtained at low amounts of corrosion inhibitors and these compounds should not be harmful to the environment.¹ Usually fatty acids are easily biodegradable compounds in nature. Therefore, fatty acids and their derivatives are widely used as anti-corrosion agents.¹⁵

In this study, as a continuation of our work related to the development of highperformance corrosion inhibitors, we have synthesized a few novel long-chain sulfurcontaining benzimidazoles. The inhibitory properties of the synthesized compounds were investigated against the corrosion of cold-rolled, low-carbon steel in 1.5-M H_2SO_4 by weight loss measurements, and further surface characterization studies were carried out. Good to excellent results were achieved with low concentrations of inhibitors.

RESULTS AND DISCUSSION

11-Bromo-N-arylundecanamides (**1a–e**) were prepared as described in the literature.¹⁶ The synthetic pathway to the preparation of the benzimidazole derivatives (**2a–e**) is shown in Scheme 1. (1*H*-Benzo[*d*]imidazol-2-yl)methanethiol and related bromo undecanamides (**1a–e**) were refluxed in acetone under nitrogen atmosphere along with potassium carbonate and the catalytic amount of sodium iodide. After crystallization from suitable solvents, compounds (**2a-e**) were obtained in high yields (Table 1).



Scheme 1 Synthesis of benzimidazole derivatives 2a-e.

The Fourier transform infrared (FT IR) and Proton Nuclear Magnetic Resonance Spectroscopy (¹H NMR) spectra confirm the structures of the synthesized compounds (Table 2). The IR spectrum of (**2a**) shows the characteristic bands for -NH stretching of amide at 3293 cm⁻¹, aromatic =C-H stretching at 3053 cm⁻¹, and carbonyl stretching (C=O) frequency of amide at 1659 cm⁻¹. The ¹H NMR spectrum showed a singlet at δ 7.54 for the amide -NH proton, signals for the three different methylene protons were Downloaded by [University of Chicago Library] at 16:04 17 November 2014

				w _i (ca w _i (fot	ulc.)/% and)/%		Yield	aW		
Compound	Formula	$M_{\rm r}$	C	Н	Z	s	%	°	Color	Crystallization solvent
2a	C ₂₅ H ₃₃ N ₃ OS	423.61	70.88	7.85	9.92	7.57	93	133-135	Yellow	EtOH
			70.41	7.83	9.51	7.07				
$2\mathbf{b}$	$C_{25}H_{32}N_4O_3S$	468.61	64.08	6.88	11.96	6.84	95	68-70	Yellow-pink	EtOH/H ₂ O/MeOH
			64.36	6.90	11.37	6.64				
2c	$C_{26}H_{35}N_{3}O_{2}S$	453.64	68.84	7.78	9.26	7.07	80	87–89	Yellow	EtOH
			68.65	7.69	8.78	6.83				
2d	C ₂₆ H ₃₅ N ₃ OS	437.64	71.35	8.06	9.60	7.33	89	129–130	White	EtOH
			71.19	7.93	9.27	7.32				
2e	C ₂₆ H ₃₅ N ₃ OS	437.64	71.35	8.06	9.60	7.33	87	69–70	Yellowish	MeOH
			71.71	8.82	8.81	7.32				

 Table 1
 Characterization data of newly prepared compounds

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Table 2 Spectral data of newly prepared comp	pounds
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Compound	Spectral data
2a	IR, $\tilde{\nu}/cm^{-1}$: 3293 (-NHCO), 3053 (aromatic =C-H), 1659 (amide C=O) ¹ H NMR (CDCl ₃), δ : 7.54 (s, 1H, -NHC=O), 7.52 (s, br, 2H, ArH), 7.38-7.37 (m, 2H, ArH), 7.34-7.30 (m, 2H, ArH), 7.28-7.24 (m, 2H, ArH), 7.10 (t, $J = 7.2$ Hz, 1H, ArH), 3.98 (s, 2H, -CH ₂ SCH ₂ CN ₂), 2.48 (t, $J = 7.6$ Hz, 2H, -CH ₂ SCH ₂ CN ₂), 2.37 (t, $J = 7.6$ Hz, 2H, -CH ₂ CONH), 1.72 (quin, $J = 8.0$ Hz, 4H, 2CH ₂), 1.53 (quin, $J = 7.6$ Hz, 2H, CH ₂), 1.35-1.20 (m, 10H, 5CH ₂)
2b	IR, $\tilde{\nu}/\text{cm}^{-1}$: 3368 (-NHCO), 3088 (aromatic =C-H), 1678 (amide C=O) ¹ H NMR (CDCl ₃), δ : 8.44 (t, $J = 2.4$ Hz, 1H, ArH), 8.01-7.99 (m, 1H, ArH), 7.95-7.93 (m, 1H, ArH), 7.57 (s, 1H, -NHC=O), 7.49-7.37 (m, 1H, ArH), 7.28-7.24 (m, 4H, ArH), 4.00 (s, 2H, -CH ₂ SCH ₂ CN ₂), 2.46 (quin, $J = 8.4$ Hz, 4H, 2CH ₂), 1.74 (quin, $J = 7.6$ Hz, 4H, 2CH ₂), 1.52 (quin, $J = 7.6$ Hz, 2H, -CH ₂ -), 1.35-1.16 (m, 10H, 5CH ₂)
2c	IR, $\tilde{\nu}/cm^{-1}$: 3288 (-NHCO), 3055 (aromatic =C-H), 1658 (amide C=O) ¹ H NMR (CDCl ₃), δ : 7.57 (s, br, 1H, -NHC=O), 7.45-7.37(m, 3H, ArH), 7.27-7.23 (m, 3H, ArH), 6.87-6.83 (m, 2H, ArH), 3.97 (s, 2H, -CH ₂ SCH ₂ CN ₂), 3.78 (s, 3H, -OCH ₃), 2.48 (t, J = 7.6 Hz, 2H, -CH ₂ SCH ₂ CN ₂), 2.35 (t, J = 7.6 Hz, 2H, -CH ₂ CONH), 1.72 (quin, J = 8.0 Hz, 2H, CH ₂), 1.52 (quin, J = 7.6 Hz, 2H, CH ₂), 1.36-1.19 (m, 12H, 6CH ₂)
2d	IR, $\tilde{\nu}/cm^{-1}$: 3305 (-NHCO), 3052 (aromatic =C-H), 1660 (amide C=O) ¹ H NMR (CDCl ₃), δ : 7.41 (s, br, 1H, -N <u>H</u> C=O), 7.39-7.37 (m, 2H, Ar <u>H</u>), 7.27-7.24 (m, 4H, Ar <u>H</u>), 7.12 (d, $J = 8.4$ Hz, 2H, Ar <u>H</u>), 3.97 (s, 2H, -CH ₂ SC <u>H₂CN₂</u>), 2.48 (t, $J = 7.6$ Hz, 2H, -C <u>H₂SCH₂CN₂), 2.35 (t, $J = 7.6$ Hz, 2H, -C<u>H₂CONH</u>), 2.31 (s, 3H, -CH₃), 1.72 (quin, J = 8.0 Hz, 2H, CH₂), 1.53 (quin, $J = 7.6$ Hz, 2H, CH₂), 1.35-1.20 (m, 12H, 6CH₂)</u>
2e	IR, $\tilde{\nu}/cm^{-1}$: 3291 (-NHCO), 3062 (aromatic =C-H), 1641 (amide C=O) ¹ H NMR (CDCl ₃), δ : 7.57 (s, br, 1H, -NHC=O), 7.37-7.32 (m, 4H, ArH), 7.30-7.23 (m, 5H, ArH), 4.46 (d, $J = 5.6$ Hz, 2H, PhCH ₂ NH-), 3.97 (s, 2H, -CH ₂ SCH ₂ CN ₂), 2.49 (t, $J =$ 7.6 Hz, 2H, -CH ₂ SCH ₂ CN ₂), 2.22 (t, $J =$ 7.6 Hz, 2H, -CH ₂ CONH), 1.65 (quin, $J =$ 8.0 Hz, 2H, CH ₂), 1.53 (quin, $J =$ 7.6 Hz, 2H, CH ₂), 1.30-1.19 (m, 12H, 6CH ₂)

obtained as a singlet at δ 3.98 for the (-CH₂SCH₂-benzimidazole), as a triplet at δ 2.48 for the (-CH₂SCH₂-benzimidazole), and as a triplet at δ 2.37 for the (-CH₂CONHAr) protons respectively.

The corrosion inhibition capabilities of the prepared compounds tested in 1.5-M H_2SO_4 acidic medium are given as percentage inhibition efficiencies, η . The observed results for (**2a–e**) inhibitors are given in Table 3. Percentage inhibition efficiencies were calculated using the following equation:

$$\eta = [(W_{\rm o} - W)/W_{\rm o}] \times 100,$$

	İnhibition efficiencies (η)					
Benzimidazoles	25 ppm	50 ppm	100 ppm	150 ppm		
2a	85	92	98	99		
2b	77	78	94	96		
2c	85	91	98	99		
2d	90	90	97	98		
2e	86	92	98	99		

Table 3 Corrosion inhibition efficiencies (η) for varying concentrations of tested benzimidazoles in 1.5 M H₂SO₄ for 5 h at room temperature (23 °C)*

*Duplicate experiments were performed in each case and the mean value of the weight loss is reported.



Figure 1 Possible orientation of inhibitor molecules 2a between the metal-acidic solution interfaces.

where η is the percentage inhibition efficiency, W_0 is the weight loss of the coupon (metal plate) in the absence of inhibitor, and W is the weight loss of the coupon in the same environment in the presence of an inhibitor compound.¹⁷

As shown in Table 3, the tested compounds showed very good inhibitory activity. Increase in inhibition efficiencies is parallel to the increase in concentration, which indicates that these compounds are adsorption inhibitors. In corrosive media, compounds are adsorbed on the metal surface through N, S, and O atoms and prevent corrosion.¹⁷ Possible orientation of inhibitor molecules (**2a**) between the metal–acidic solution interfaces is shown in Figure 1. As can be seen, molecules are found in an upright position in the metal surface. Such a position provides maximum protection. In addition, the following statements can be made which are supported with Figure 2: Part of the molecules (**2a**)



Figure 2 Formation of secondary molecular layer.



Figure 3 Interactions at low inhibitor concentrations.

adsorbed on the metal surface via S atom and benzimidazole ring, other molecules are connecting on the metal surface still with S atom and π - π interactions between aromatic rings also takes place. In addition, intermolecular H-bonds are formed via amide groups, which increase the stability of the protective layer. Increase in inhibition activities due to increase in inhibitor concentrations may indicate that a secondary molecular layer can occur (bilayer) via H-bonds and Van der Waals forces.¹⁸⁻²⁰

At low inhibitor concentrations, probably both ends of the molecule interact with the metal surface to provide protection as shown in Figure 3. The horizontal orientation of inhibitor molecules on the surface of the metal prevents the growth of the secondary molecular layer. In addition, the presence of electron withdrawing $-NO_2$ group in inhibitor (**2b**) decreases its effectiveness, which proves that the interaction via amide end of the molecule is also possible. As a result, a slightly lower inhibition was observed.

Typically, the chemical composition of the metal surface changes after the adsorption of inhibitor molecules, which also changes the surface wettability. The characteristics of the metal surface (hydrophilic or hydrophobic) can be determined indirectly by the water contact angle (WCA) measurements. Static water contact angle measurements observed at 150-ppm inhibitor concentration are given in Table 4. The WCA measurements support η values, which are calculated from the observed weight loss measurements given in Table 3. Similar WCA and η values were observed for **2a**, **2c**, **2d**, and **2e** compounds. As can be seen from the tables, the lowest η and WCA values were obtained for the inhibitor (**2b**). These two values compliant with each other, supports the mechanism of inhibition that is recommended above for this compound.

The 3D optical profilometer images of some metal coupon surfaces are given in Figure 4. The photos were taken from the surface at $100 \times$ magnification. As seen from images in Figure 4, the treatment of the metal coupon to acidic medium without inhibitor leads to corrosion damages on the metal surface, while the treatment of the metal coupon with inhibitor prevents the corrosion of the surface.

Table 4 Static water contact angle measurements on the metal surface that immersed in $1.5 \text{ M} 100 \text{ mL H}_2\text{SO}_4$ solution containing one of the inhibitors 2a, 2b, 2c, 2d or 2e at 150 ppm concentration

Measured contact angles (Average values)							
Inhibitors	Blank	2a	2b	2c	2d	2e	
	43.70 ± 0.19	69.78 ± 2.17	59.26 ± 0.18	67.25 ± 1.21	65.78 ± 2.58	68.80 ± 3.99	



Figure 4 3D optical profilometer images of the metal coupon surface.

CONCLUSIONS

The results of corrosion tests are quite satisfactory. The synthesized long-chain alkylthia-benzimidazole derivatives exhibited the highest inhibition at 150-ppm inhibitor concentration. In parallel with increase in inhibitor concentration, the observed adsorption layer provides better protection. The results obtained from gravimetric tests and other measurements indicate that these compounds are suitable anti-corrosion agents for carbon steel in 1.5-M H_2SO_4 .

EXPERIMENTAL

All reagents and solvents were purchased from either Merck or Fluka Chemie, and were used without further purification. Melting points were recorded by BÜCHI melting point B-540 apparatus. IR spectra were measured by Nicolet FT IR 6700 spectrometer. ¹H NMR spectra were measured using Varian mercury plus spectrometer (400 MHz) in deuterochloroform (CDCl₃) using tetramethylsilane (TMS) as an internal standard.

(1H-Benzo[d]imidazol-2-yl)methanethiol was prepared according to the procedure reported in the literature²¹ but with some modifications. A solution of o-phenylenediamine (9.45 g, 87.4 mmol) and thioglycolic acid (19.8 g, 215 mmol) in 4-M HCl (100 mL) was refluxed under nitrogen for 1.5–2 h. The green reaction mixture was then cooled to 0 °C in an ice bath, maintaining the temperature of the mixture below 5 °C; the pH of the reaction mixture was adjusted to 7.0 by slow addition of concentrated ammonia solution. After precipitation from the solution was completed, the grey-white solid was collected, typically by vacuum filtration and dried at room temperature overnight. The crude product was crystallized from 50% EtOH with cautiously heating under nitrogen. The pink-grey needle crystals were collected by vacuum filtration and dried in vacuum desiccator over CaCl₂, (8.5 g, 59%), mp 156–157 °C. This compound was used without further characterization.

General Procedure for the Preparation Benzimidazole Derivatives (2a-e)

In a 100-mL round bottom flask fitted with a reflux condenser, acetone (30 mL), (1H-benzo[*d*]imidazol-2-yl)methanethiol (1 g, 6.09 mmol), K_2CO_3 (1 g, 7.24 mmol), and NaI (0.1 g, 0.67 mmol) were placed. The resulting mixture was heated in a water bath for 10–15 min under nitrogen. Thereafter 11-bromo-N-benzyl or 11-bromo-N-arylundecanamide (6.17 mmol) was added and flask was heated to reflux in a water bath and refluxed for 5–6 h under nitrogen. After the amide was consumed (checked by TLC), the acetone was removed by a rotary evaporator under reduced pressure and the residue was dissolved in CHCl₃. The chloroform solution was washed with water, dried with anhydrous Na₂SO₄, and concentrated under vacuum. The observed residue was purified by crystallization or column chromatography.

Corrosion Tests Performed in 1.5-M H₂SO₄

Coupons were prepared according to the method previously described in the literature.¹⁷ The coupons are made from cold rolled low-carbon steel with the composition of 0.07% C, 0.35% Mn, 0.015% P, and 0.015% S, and were cut in rectangular shapes of $0.1 \times$ 2.2×5.0 cm in thickness, width, and length respectively. A solution of 1.5-M H₂SO₄ was prepared from concentrated H₂SO₄ (98%) (Merck grade). Mass loss measurements were performed as follows. Inhibition efficiencies of (2**a–e**) benzimidazoles were tested at 25, 50, 100, and 150 ppm concentration in 100 mL of 1.5-M H₂SO₄ solution. The synthesized inhibitors were added into the acidic solution as dissolved in 10% acetone. However, some solutions are not clear. Later the treatment solutions were poured into 150 mL of sealed glass bottles and the coupons were suspended into these solutions without stirring and kept for 5 h at room temperature (23°C). Control tests were done in the same way without inhibitors. After the corrosion test, the samples were treated as follows: coupons were taken out and wiped with paper tissues. The coupons were gently polished with emery paper to clean the rust as needed, rinsed with water then acetone, and dried in an oven to a constant weight.

Contact Angle Measurements

The contact angles of the metal coupon surfaces were determined with the KSV Attention Tetha (Hamburg, Germany) instrument. The contact angle of the surfaces was measured with the Sessile Drop method by dropping one water drop. Ten separate photos were taken from different parts of surfaces, and contact angle values were measured for each drop. Measured contact angle values were obtained as the left contact angle, the angles from the left contact point of the droplet with solid and right contact angle from the right contact point. In addition, average contact angle values were the average of 10 measurements.

Optical Profilometer Images

In order to characterize the surface of metal coupons, Zeta-20 True Color 3D Optical Profiler (Zeta Instruments, CA, USA) was used. Sample was mounted on sample holder under the objective and the photos were taken from the surface at $100 \times$ magnification.

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