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A Bis(di-*n*-butyltin)–Quinone Derivative as a Simultaneous Chemo- and Bioactive Corrosion Inhibitor

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The bis(di-*n*-butyltin) derivative of 2,5-bis(2-hydroxyethylamino)-1,4-benzoquinone was synthesized and characterized by common spectroscopic techniques. In solution, discrete molecules with pentacoordinate tin atoms were observed, whereas the X-ray diffraction analysis of the solid-state structure revealed polymeric chains that were due to intermolecular Sn···O bonds. In vitro tests demonstrated that the tin compound displays bactericidal activity against a wide range of aerobic and anaerobic bacteria. Acute toxicity tests indicated that the di-*n*-butyltin compound has a relatively low toxicity level. The corrosion inhibition efficiency of the ligand and the tin compound were evaluated by polarization scans of mild steel samples that had been exposed to a sour brine environment. The tin–quinone compound showed good inhibition efficiency (about 75 %) at relatively low concentrations (25–50 ppm) and at different testing times (0.25–20 h).

Introduction

At present, organic compounds are widely used as corrosion inhibitors, since their structural features can be manipulated in order to improve properties such as solubility and chemical biodegradability. For that purpose, the formation of strong coordinative bonds with metallic surfaces is required, in particular in the very aggressive media present in oil manufacturing plants and pipelines. In this respect, nitrogen-based inhibitors have demonstrated excellent properties.[1]

It is well known that ligands based on quinones confer the ability to couple redox reactions, thus enabling the interaction with metallic ions and surfaces.[2] Earlier studies have shown that metal surfaces covered with poly(aminoquinones) (PAQs) form effective anticorrosive coatings because of their excellent corrosion resistance and adhesion to metal atoms.[3] Such films even displace water from rusted steel surfaces.[4] Hubbard and co-workers have attributed the high affinity of PAQs towards metal surfaces to a chemisorption process[5] in which the free electron pairs of the amine nitrogen and quinone oxygen atoms interact with the electron-deficient molecular orbital of the metal atom. Surprisingly, so far there is no reference related to the use of organometallic components containing benzoquinones as corrosion inhibitors for steel, and the manner in which coordination to metal atoms influences the corrosion inhibition properties has not been clarified yet.

Tin phthalocyanines were previously tested as corrosion inhibitors for carbon steel by using sour brine at pH 4.[6] The corrosion inhibition activity of these compounds provided efficiencies in the range 61–87% at concentrations of 500 ppm, and it was proposed that the concave π-electron-delocalized nanocap morphology of these compounds may induce an effective adsorption on the steel surface. In addition, tin compounds are capable of acting as biocides and have relatively low toxicities,[7] thus making them an attractive object of research for the development of chemicals having combined anticorrosive and antibacterial properties. This is because anaerobic bacteria are able to catalyze the corrosion processes in oil plants and pipelines.

Our interdisciplinary research group is interested in developing evironment-friendly multifunctional compounds, and, we describe herein the synthesis and properties of a new di-*n*-butyltin derivative of 2,5-bis(2-hydroxyethylamino)-1,4-benzoquinone (**1**). As far as we know, this is

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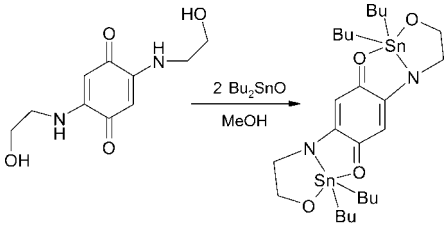
the first report on a tin compound that is able to protect steel simultaneously from electrochemical and microbiological corrosion.

Results and Discussion

The 1,4-benzoquinone derivative **1** was prepared as described previously,[8] and its condensation reaction with di-*n*-butyltin oxide in methanol under reflux gave compound **2** in 80% yield (Scheme 1). Recrystallization of the product from methanol gave a deep red crystalline material. EI mass spectrometry revealed a peak at m/z = 688 that corresponds to the molecular ion of compound **2**. The analysis of the ^{1}H NMR spectroscopic data suggests that the structure of this compound is symmetric in solution, having a C_2 rotation axis. By using the equation developed by Holeček et al.,[9] the $^1J(^{119}Sn–^{13}C)$ coupling constant (628 Hz) was used to estimate the C–Sn–C angle, 127.4°, which is typical of pentacoordinate tin species. The ^{119}Sn NMR chemical shift was observed at δ = –129 ppm, a value displaced to higher frequencies relative to parent diorganotin compounds derived from ONO Schiff base tridentate ligands (–150 to –180 ppm).[10] The difference can be attributed to the enhanced covalent character of the N–Sn bond that is mostly dative in analogous systems.



1 **2**

Scheme 1. Synthesis of the tin–quinone compound **2**.

The X-ray analysis of compound **2** allowed to establish that in the solid state the point group of the tin molecules is C_1 (Figure 1). When the molecular packing was examined, intermolecular Sn···O interactions were found, providing hexacoordinate tin atoms that are surrounded by the ONO donor atoms of one ligand molecule (meridional distribution), two *n*Bu groups located in a *trans* orientation, and one additional oxygen atom from a neighboring molecule. The *n*-butyl groups attached to the tin atoms and the –CH_2CH_2O– fragments of the ligand are disordered over two different positions, indicating the presence of a low-density polymorphous arrangement. The N–Sn and O–Sn bond lengths are comparable to those already described for other ONO–tin compounds (for values see Figure 1).[10,11]

The formation of intermolecular Sn···O bonds, 2.488(6) (O2–Sn2) and 2.379(4) (Sn1–O3A) Å, situated at an equatorial position of the tin atom coordination sphere, gives rise to the formation of four-membered Sn_2O_2 rings that organize the individual molecules in linear 1D coordination polymers (Figure 2). This Sn···O intermolecular interaction

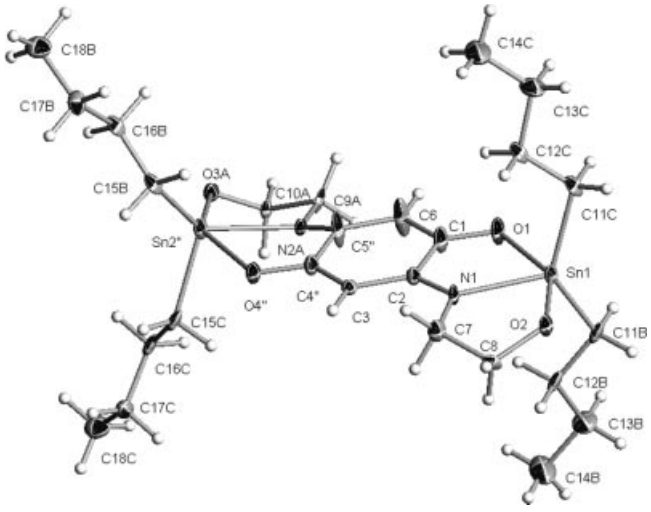


Figure 1. Fragment of the polymeric structure of compound **2** (50% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Sn1–O1 2.336(5), Sn1–O2 2.092(4), Sn1–N1 2.172(5), Sn1–C11B 2.1011(11), Sn1–C11C 2.1003(11), O1–Sn1–O2 147.17(16), O1–Sn1–N1 70.66(18), O2–Sn1–N1 76.51(19), C11C–Sn1–C11B 140.7(3).

has also been observed for other pentacoordinate di-*n*-butyltin complexes derived from ONO ligands.[12] The polymeric fragments are organized in layers, between which the *n*Bu moieties are located (Figure 2).

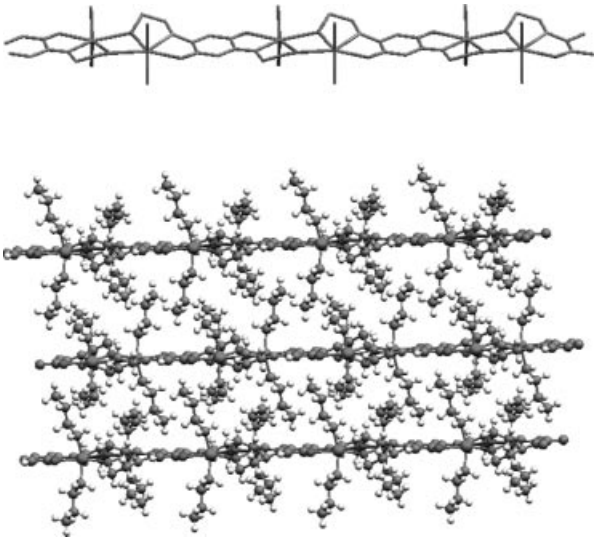


Figure 2. Schematic representation of the 1D coordination polymer formed through Sn···O intermolecular interactions (part of the *n*Bu groups are omitted, top). View of the parallel orientation for the polymeric chains, the *n*Bu groups are located in between (bottom).

The benzoquinone ligand **1** and the bis(di-*n*-butyltin)–quinone derivative **2** were screened in vitro for their antibacterial activity against three types of aerobic bacteria, *Bacillus subtilis* (Gram-positive, strain ATCC 6633), *Escherichia coli* (Gram-negative, strain DH5) and *Pseudomona fluorescens* (Gram-negative, strain BH3), and two types of anaerobic species (sulfate-reducing bacteria, SRB), *Desulfovibrio vulgaris* (strain DSM 644) and a bacteria con-

sortium (strain 82) isolated from a hydrocarbon pipeline of the Mexican oil industry (PEMEX). The agar well diffusion method[13] was used to determine the minimum inhibitory concentrations (MICs), showing that compound **2** has a higher biocide activity than the free quinone **1** (Table 1). The results also show that the presence of the di-*n*-butyl group confers selectivity in toxicity against certain bacterial species, which is important for the development of new prototypes of environmentally friendly biocides.

Table 1. Agar MICs of compounds **1** and **2** (ppm).[a]

Compound	*B. subtilis*	*E. coli*	*P. fluorescens*	*D. vulgaris*	*Strain 82*
1	≥ 200	≥ 200	≥ 200	> 200	> 200
2	10	100	10	≥ 100	150

[a] For *B. subtilis*, *E. coli*, and *P. fluorescens*, the MICs were measured after 16 h of incubation at 30 °C. For *D. vulgaris* and *Strain 82* the MICs were measured after 7 days of incubation at 32 °C.

The acute toxicity was determined by using luminescent bacteria toxicity (LBT) Mycrotox tests to record their environmental impact. The EC_{50} values obtained from 5- and 15-min assays were very similar for the two compounds (Table 2), which permits their classification in the "slightly toxic" category.[14]

Table 2. Acute toxicity of compounds **1** and **2** against *P. phosphoreum*.[a]

Compound	Toxicity EC_{50}		
	5 min	15 min	Category
1	61	58	slightly toxic
2	62	60	slightly toxic

[a] Concentration range in ppm, classification, category 5: 0.01–0.10, extremely toxic; 4: 0.1–1.0, highly toxic; 3: 1–10, moderately toxic; 2: 10–100, slightly toxic; 1: 100–1000, particularly nontoxic; and 0: > 1000, nontoxic. See ref.[14] for further details.

The carbon steel corrosion inhibition properties of compounds **1** and **2** were tested in an aqueous hydrogen sulfide corrosive environment by electrochemical methods, which included the linear polarization resistance (LPR) technique and the Tafel extrapolation measurements. Upon electrode immersion for 15 minutes in sour brine at different inhibitor concentrations, the corrosion inhibition efficiencies of the benzoquinone ligand **1** were in the range 37–61%, whereas those of compound **2** were within 35–83%. The detailed analysis of the data shown in Table 3 shows that compound **2** is a better corrosion inhibitor than **1**, since a molar concentration of only one third of compound **2** is required to provide a higher inhibitive efficiency than that of compound **1**. After 20 h of electrode immersion, the results show that the inhibition efficiency of compound **1** tends to increase slightly, while that of compound **2** tends to decrease. There exists some evidence that planar compounds such as **1** give a parallel accommodation on the steel surface due to π-bonding interactions with the metal atoms.[2] In the case of compound **2**, the molecular volume is increased, which apparently improves the surface coverage.[15] The inhibition efficiencies of this new di-*n*-butyltin compound are in the order of those found for the tin phthalocyanines previously reported;[6a] however, the inhibitor concentration is five times lower.

Table 3. Corrosion inhibition efficiency (IE,%) for compounds **1** and **2**.

Compound	Concentration		IE (%)	
	ppm	mmol L^{-1}	[a]	[b]
1	10	0.0442	37	15
	25	0.1100	57	69
	50	0.2210	55	74
	100	0.4420	61	66
2	10	0.0145	35	8
	25	0.0363	82	66
	50	0.0726	87	70
	100	0.1453	83	72

[a] IE determined after 15 min. [b] IE after 20 h.

Conclusion

The tin compound described herein can protect steel surfaces by serving as a chemo- and bioactive corrosion inhibitor. Further investigations considering similar tin–quinone derivatives are currently carried out in our laboratory.

Experimental Section

Synthesis and Spectroscopic Data for Compound 2: Compound **2** was prepared from compound **1** (0.10 g, 0.442 mmol) and di-*n*-butyltin oxide (0.22 g, 0.884 mmol) in methanol under reflux (2 h). The product precipitated as a red solid in 80% yield (0.24 g). M.p. 247–250 °C. IR (KBr): $\tilde{\nu}_{max}$ = 2956, 2921, 2854, 1523 (C=O), 1433, 1398, 1329, 1288, 1066, 920, 872, 800, 680, 593 cm^{-1}. EI-MS: *m*/*z* (%) = 688 [M^+] (10), 661 (45), 632 [M – Bu]$^+$ (100), 604 (33), 543 (24), 513 (12), 486 (56), 400 (60), 371 (45), 280 (34), 203 (64), 174 (43), 123 (17), 91 (26). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.61 (s, 2 H, CH), 3.96 and 3.30 (AB, J = 5.8 Hz, 8 H, OCH_2CH_2N), 1.60–1.16 (m, 24 H, CH_{2Bu}), 0.82 (t, J = 6.9 Hz, 12 H, CH_{3Bu}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$), δ: 181.0 (C=O), 151.1 (C_{quin}–N), 93.3 (C–H), 61.6 (C_{aliph}–O), 48.2 (C_{aliph}–N), 27.5 [^2J(^{119}Sn–^{13}C) = 29 Hz, $C_{\beta\text{-Bu}}$], 26.9 [^3J(^{119}Sn–^{13}C) = 87 Hz, $C_{\gamma\text{-Bu}}$], 19.7 [^1J(^{119}Sn–^{13}C) = 628 Hz, $C_{\alpha\text{-Bu}}$], 13.8 ($C_{\delta\text{-Bu}}$) ppm. ^{119}Sn NMR (75 MHz, $CDCl_3$): δ = –129 ppm. $C_{26}H_{46}N_2O_4Sn_2$ (688.07) calcd. C 45.38, H 6.73, N 4.07; found C 46.01, H 6.86, N 4.22.

Antibacterial Activity Test: The agar method was used to determine the minimum concentration of compound **1** and **2** capable of inhibiting the bacterial activity of the aerobic and anaerobic strains previously developed. The medium for the aerobic bacteria was prepared by cooling the molten agar to 40 °C and then adding the required amount of bacterial suspension (8×10^8 bacteria per mL). The wells were dug in the media with the help of a sterile metallic borer of 24 mm diameter; into these wells the testing compounds were introduced (2.5, 10, 25, 50, 75, 100, 150 and 200 ppm). Additional wells were filled with ethanol to serve as a negative control, whereas the positive reference was a piperazine compound. The flat-bottomed, 90-mm Petri dishes were kept at 4 °C for 60 minutes and then stored in an incubator at a suitable growth temperature (30 ± 2 °C) for 16 hours. The strains prepared for the anaerobic bacteria were exposed to the testing compounds in the range 2.5–200 ppm, whereby the anaerobic strains were grown in 40-mL

flasks with a Postgate C modified medium. The bottles were inoculated with SRB (sulfate-reducing bacteria) cultures (1 mL) from the stock and incubated at 32 ± 2 °C for 7 d. Finally, the minimum inhibitor concentration (MIC) for each compound was determined by comparing positive (bottle without chemical) and negative (bottle not inoculated with culture) controls and recording the presence or absence of visible growth in the bottles.

X-ray Crystallography: X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector, Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator. Frames were collected at T = 100 K. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT).[16] Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package.[16] Crystal system: Monoclinic, space group $P2_1/m$, a = 6.9974(7), b = 17.3487(17), c = 11.7734(12) Å, β = 91.799(2), V = 1428.5(3) Å^3, Z = 4, $D_{calcd.}$ = 1.604 g cm^{-3}, μ = 1.781 mm^{-1}, $F(000)$ = 700. For 2319 independent reflections and 245 parameters, final R indices [$I > 2\sigma I$]: R_1 = 0.0370 and wR_2 = 0.0825. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions by using a riding model. The *n*Bu groups attached to the tin atoms and the –CH_2CH_2O– fragments of the ligand are disordered over two positions. CCDC-296858 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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