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Electrochemical Property and Formation of the Cation Radical and Dication of Dinaphtho[1,8-*b*,*c*]-1,5-dithiocin

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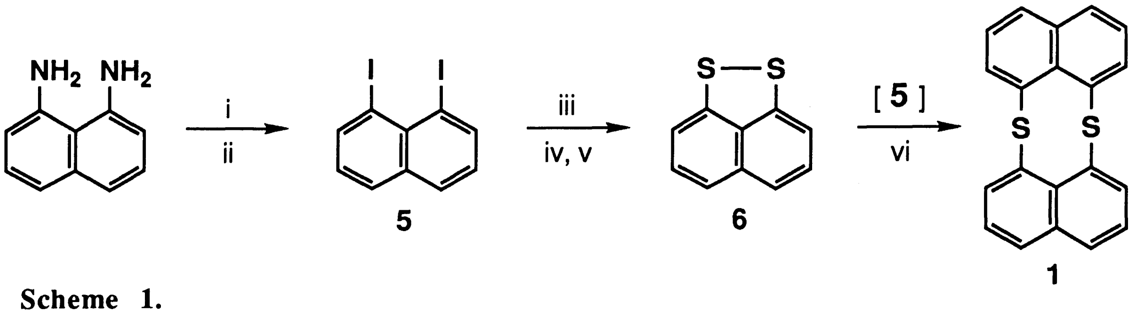
A new symmetrical dithio *peri*-bridged naphthalene, dinaphtho[1,8-*b*,*c*]-1,5-dithiocin (**1**) has been synthesized. The cyclic voltammogram of **1** showed one reversible oxidation peak. ESR spectrum of the concd H_2SO_4 solution of **1** showed the formation of the cation radical. The formation of the dication of **1** was observed in the reaction of the corresponding monosulfoxide with concd D_2SO_4 by both high-field ^{1}H and ^{13}C NMR spectroscopy.

Although chemistry of cation radicals of heterocyclic compounds has been under discussion for some time,[1,2] the preparations and reactions of the corresponding dications are little known.[1b,d] We have recently reported the preparation, structure, and reactivity of σ-bonded dications in aliphatic medium-sized cyclic compounds containing multi-sulfur and -selenium atoms.[3] On the other hand, the reactivities of the aromatic cation radical of thianthrene have been extensively studied, in which its cation radical is stabilized by conjugation with aromatic rings.[2] More recently, we have synthesized dinaphtho[1,8-*b*,*c*]-1,5-dithiocin (**1**) as a non-planar aromatic molecule which possesses the possibilities of the intramolecular sulfur-sulfur interaction, and the interaction between the p-orbitals of the sulfur atoms and the naphthalene π-system. We now report herein the synthesis, electrochemical reversible oxidation, and formation of the cation radical and the dication of a new aromatic compound containing sulfur atoms **1**.

The bis-sulfide **1** was synthesized as follows (Scheme 1). 1,8-Diiodonaphthalene (**5**) and naphtho[1,8-*c*,*d*]-1,2-dithiole (**6**) were prepared according to the method reported in the literature.[4,5] To a solution of disulfide **6** (0.55 g, 3.0 mmol) and sodium hydride (NaH; 0.29 g, 7.25 mmol) in hexamethylphosphoric triamide (HMPA; 20 ml) was added CuI (1.14 g, 6.0 mmol) under a nitrogen atmosphere. Then the compound **5** (1.10 g, 3.0 mmol) was added to this mixture. The whole mixture was stirred at 100 °C for 8 h. After the usual

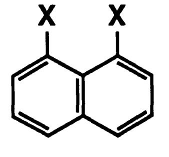


Scheme 1.

Reagents: i, H_2SO_4, $NaNO_2$; ii, KI; iii, n-BuLi in THF; iv, S_8; v, $LiAlH_4$; vi, NaH, CuI in HMPA.

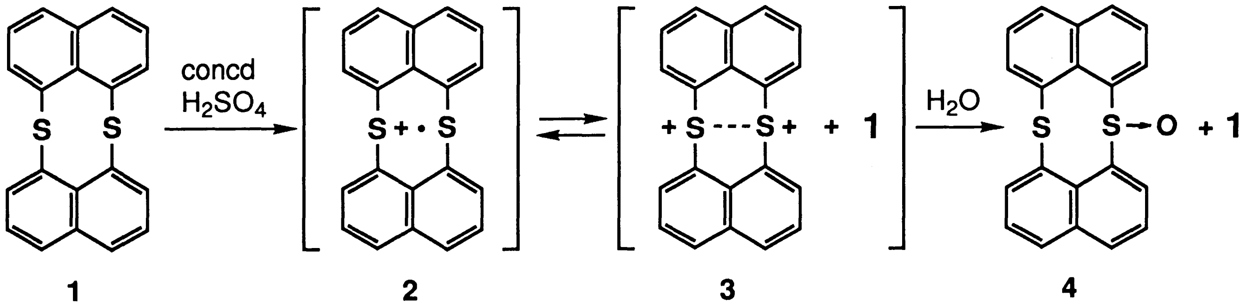
work-up the crude products were purified by silica-gel column chromatography (eluent, hexane) to give **1** in 39% yield. The compound **1** was recrystallized from hexane, mp 262-263 °C.[6)]

The electrochemical oxidation of bis-sulfide **1** was studied by cyclic voltammetry. Interestingly, when the cyclic voltammogram of **1** was measured in CH_3CN-0.1 M $NaClO_4$ with a glassy-carbon working electrode and Ag/0.01 M $AgNO_3$ in CH_3CN as a reference electrode (scan rate; 200 mV/s), one *reversible* oxidation peak appeared at the oxidation potential, +0.70 V ($E_{1/2}$ = +0.66 V), and the second wave was irreversible. However, the analogous compounds of **1**, 1,8-bis(methylthio)naphthalene (**7**), naphtho-[1,8-*b*,*c*]-1,5-dithiocin (**8**), and di-1-naphthyl sulfide show the irreversible redox behavior in all steps.[7)] These results suggest that the cationic species of **1** generated at electrode is more stabilized than those of **7** and **8**. A peak potential of **1** is about 450 mV more cathodic than that of thianthrene (Th).[8)] That is, **1** should be more readily oxidized.



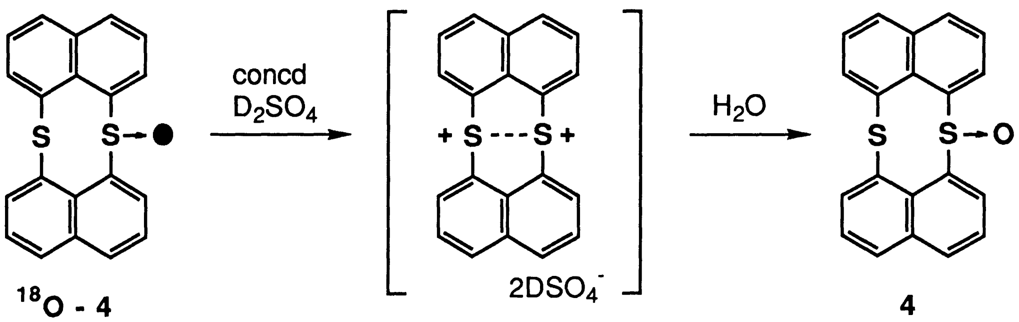
7: X= -SMe
8: X= $-S(CH_2)_3S-$

When bis-sulfide **1** was dissolved in concentrated H_2SO_4 (98%) at room temperature, the solution became green.[9)] This H_2SO_4 solution gave an ESR signal with *g* = 2.0092 which can be attributed to the cation radicals containing sulfur atoms. Treatment of H_2SO_4 solution of **1** with ice-H_2O and work-up afforded quantitatively the mono-sulfoxide **4** and the sulfide **1** in a 1:1 ratio (Scheme 2).[10)] The mechanism for formation of sulfoxide **4** and sulfide **1** can be explained as follows; the water reacts with the dication **3**, formed by disproportionation of the cation radical **2**, rather than with the cation radical itself.[9)]



Scheme 2.

Dissolution of mono-sulfoxide **4** in concd D_2SO_4 (98%) at room temperature resulted in a purple colored solution. The ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra of D_2SO_4 solutions of **4** were recorded immediately; the aromatic proton signals observed in $CDCl_3$ for **4** disappeared and three sets of new peaks appeared at lower field, δ 8.65 (d, 4H), 8.29 (d, 4H), and 7.94 (t, 4H), while the ^{13}C NMR spectra also showed the analogous changes (Table 1 and Scheme 3). The spectra did not change for several weeks at room temperature. These results indicate that **4** is converted into the symmetrical intermediate dication **3**. Hydrolysis of the D_2SO_4 solution of **4** led to 91% recovery of the *S*-oxide, and none of the sulfide **1** was obtained. In contrast to **4**, hydrolysis of a solution of thianthrene mono-sulfoxide (Th=O) in concd H_2SO_4 afforded at least three products, i.e., Th, Th=O, and 2-hydroxythianthrene sulfoxide;[11)] these results suggest that the positive charges of the cation radical and/or dication of Th in H_2SO_4 should be delocalized in the aromatic rings, and subsequently a H_2O molecule attacks both the sulfur and the carbon atoms in the aromatic ring. These findings suggest that a positive charge developed on the one sulfur atom of **1** is more delocalized to the other sulfur atom than to the naphthalene ring.



^{18}O - 4 (● = ^{18}O)

Scheme 3.

3

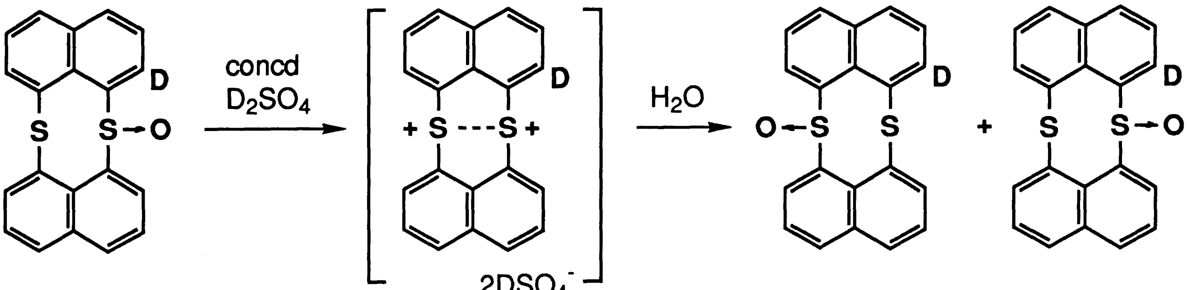
4 (^{18}O = 0 %)

Table 1. NMR Data for **1**, **3**, and **4**[a)]

	Chemical shift, δ ^1H	^{13}C[b)]
1	8.12 (d, *J*=8 Hz, 4H), 7.79 (d, *J*=8 Hz, 4H), 7.37 (t, *J*=8 Hz, 4H)	137.2 (1), 136.0 (0), 135.0 (0), 134.2 (0), 131.1 (1), 125.9 (1)
4	8.59 (d, *J*=8 Hz, 2H), 8.03 (d, *J*=8 Hz, 2H), 7.84 (d, *J*=8 Hz, 2H), 7.79 (d, *J*=8 Hz, 2H), 7.61 (t, *J*=8 Hz, 2H), 7.42 (t, *J*=8 Hz, 2H)	147.3 (0), 135.9 (1), 135.7 (0), 133.2 (0) 132.5 (0), 130.7 (1), 130.5 (1), 126.6 (1), 126.5 (1), 123.4 (1)
3	8.65 (d, *J*=7 Hz, 4H), 8.29 (d, *J*=7 Hz, 4H), 7.94 (t, *J*=7 Hz, 4H)	148.6 (0), 139.2 (0), 138.1 (1), 133.9 (1),133.7 (1), 129.7 (0)

a) ^1H and ^{13}C NMR data for **1** and **4** in $CDCl_3$; for **3** in concd D_2SO_4. b) In cases where DEPT experiments were carried out during ^{13}C NMR experiments, the carbon multiplicities are listed as (0) quaternary, (1) methine.

In order to confirm the oxygen exchange by an ^{18}O tracer experiment, ^{18}O-labeled sulfoxide ^{18}O-**4** (23% ^{18}O excess)[12)] was prepared and dissolved in concd H_2SO_4. Upon treatment with ice-H_2O, no ^{18}O was found in the recovered *S*-oxide (confirmed by mass spectrometry) (Scheme 3). This result clearly demonstrates that the oxygen-exchange reaction actually took place *via* the formation of dication **3**, namely the intra- and/or intermolecular oxygen-transfer reactions between sulfoxides and sulfides in acidic solutions were ruled out.



$2DSO_4^-$

4a Scheme 4.

4b 4a

Further mechanistic evidence for the formation of the dication **3** was gained using α-deuteriated sulfoxide **4a** which was prepared by reaction of lithio-derivative of **4** with D_2O.[13)] Similar treatment of **4a** in concd D_2SO_4 led to analogous changes in the ^1H NMR spectra and only mono-sulfoxide was obtained by hydrolysis of the D_2SO_4 solution. The ^{1}H NMR spectrum of the mono-sulfoxide obtained indicated that it was a 1:1 mixture of **4a** and the deuteriated isotopomer **4b** and also that no H-D exchange with the solvent H_2SO_4 took place during the reaction (Scheme 4). This result also reveals the formation of the symmetrical dicationic species.

The results described herein show the remarkably stable oxidized ions, cation radical and dication, of a new non-planar aromatic compound containing sulfur atoms. The cyclic voltammetry of **1** exhibits that **1** may become a new type of an electron donor molecule. We are continuing the studies on the synthesis and properties of its derivatives containing selenium and tellurium atoms.

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6) Compound **1**: mp 262-263 °C; MS, *m/z* 316 (M^+). Anal. Found: C, 75.84; H, 3.79; S, 20.32%. Calcd for $C_{20}H_{12}S_2$: C, 75.91; H, 3.82; S, 20.27%.

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10) Compound **4**: mp 317-318 °C; FT-IR (KBr) 1044 cm^{-1} (SO). Anal. Found: C, 72.33; H, 3.61%. Calcd for $C_{20}H_{12}OS_2$: C, 72.26; H, 3.64%.

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12) The reaction of sulfide **1** with nitrosonium hexafluorophosphate ($NO^+PF_6^-$) as a one-electron oxidizing agent in anhydrous CH_3CN-CH_2Cl_2 gave the solid, which on treatment with $H_2{}^{18}O$ (≈90 atom %) resulted in the formation of ^{18}O-labeled compound ^{18}O-**4**. The ^{18}O content was 23 atom % by mass spectrometery.

13) The lithiation of sulfoxide **4** was performed by using an equimolar amount of lithium diisopropylamide (LDA) in anhydrous THF at -78 °C. The lithiation took place only at the α-position of the sulfinyl group in **4**. The lithio-derivative generated was treated *in situ* with D_2O at -20 °C to give the α-deuteriated mono-sulfoxide **4a** (D-content was >95 atom %).

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