Generation and Detection of a Dithia Dication Derived from 4,9-Diethyl-[1,4]dihydrodithiino[5,6-*f*]benzotrithiole 5-Oxide and Its Disproportionation

Takeshi Kimura,*[†,††] Shinya Ito,[††] Takashi Sasaki,[††] Shigeya Niizuma,[†††] Satoshi Ogawa,[††] Ryu Sato,[††] and Yasushi Kawai[††††]
[†]*Center for Instrumental Analysis, Iwate University, Morioka 020-8551*
[††]*Department of Chemical Engineering, Faculty of Engineering, Iwate University, Morioka 020-8551*
[†††]*Faculty of Humanities and Social Science, Iwate University, Morioka, Iwate 020-8550*
[††††]*Institute for Chemical Research, Kyoto University, Uji 611-0011*

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A dithia dication was generated from 4,9-diethyl[1,4]-dihydrodithiino[5,6-*f*]benzotrithiole 5-oxide on treatment with D_2SO_4. Hydrolysis of the dication gave 4,9-diethyl[1,4]dihydrodithiino[5,6-*f*]benzotrithiole 1-oxide and 2-oxide, suggesting that the positive charges, generated on the dithiin ring, transferred to the trithiole ring. A disproportionation of the dithia dication was observed in the solution.

Since Wolmershäuser reported the first isolation of a benzotriselenole radical cation in 1992,[1] several interesting radical cation and diradical dication derivatives were prepared on treatment of benzotrichalcogenoles with $NOPF_6$ and $SbCl_5$.[2,3] On the other hand, a molecule bearing both sulfinyl and sulfenyl groups in close proximity, gave a corresponding dithia dication by deoxygenation with H_2SO_4, and the dithia dication was stabilized by through space interaction between two sulfur atoms.[4–7] If a trithiole ring is appropriately fused to that molecule, the dithia dication generated is expected to interact with the trithiole ring electronically. Thus 4,9-diethyl[1,4]dihydrodithiino[5,6-*f*]benzotrithiole 5-oxide (**2**) was prepared by oxidation of 4,9-diethyl[1,4]dihydrodithiino[5,6-*f*]benzotrithiole (**1**) and was treated with H_2SO_4. This paper reports the generation, detection, charge transfer and disproportionation of a dithia dication derived from **2**.

As a preliminary experiment, **1** was treated with two equivalent of $NOPF_6$ at −78 °C and then with water.[8] By this reaction, 4,9-diethyl[1,4]dihydrodithiino[5,6-*f*]benzotrithiole 1-oxide (**3**) and 2-oxide (**4**) were obtained in 70% and 13% yields, respectively.[9] Interestingly, **2** was not detected at all in this oxidation reaction,[10] suggesting that the positive charges, generated by oxidation of **1** with $NOPF_6$, localize on the trithiole ring not on the dithiin ring, and the trithiole ring has higher acceptability of the positive charge than the dithiin ring.[11] Therefore, if the positive charge is generated on the dithiin ring of **1**, that is predicted to transfer from the dithiin ring to the trithiole ring. For instance, **2** is expected to produce a dithia dication on the dithiin ring, initially, by deoxygenation with H_2SO_4 and a transannular interaction between two sulfur atoms. For a selective generation of two positive charges on the dithiin ring, **2** was dissolved in D_2SO_4 at room temperature and then the solution was examined by ^{1}H-NMR spectroscopy (Figure 1). The solution became initially dark-purple color, and then changed to dark-green color in a few minutes. In the ^{1}H-NMR spectrum of **2** measured in $CDCl_3$, double quartet, quartet, and two triplet signals were observed for two ethyl groups, and the methylene protons of the dithiin ring were recorded as four *ddd* signals (Figure 1-a). Contrastively, the spectrum measured in D_2SO_4 exhibited three somewhat broad signals (Figure 1-b), which show that the species generated has a symmetric structure in D_2SO_4. When the dark-green colored D_2SO_4 solution was treated with ice water, formation of **3** and **4** were observed as major products. So we tried to determine the products and their yields in detail; hence, **2** was dissolved in H_2SO_4, and then the solution was treated with ice water to give **3** and **4** in 41% and 20% yields, respectively, together with **1** (17%), **5** (17%) and recovered **2** (2%) (Scheme 1). Meanwhile, the ^{1}H-NMR signals of **2** in D_2SO_4 disappeared slowly on broadening of them. Thus the reaction of **2** with H_2SO_4 was followed by ESR spectroscopy at 10 °C. In the spectrum, one broadening strong signal was recorded at $g = 2.017$.

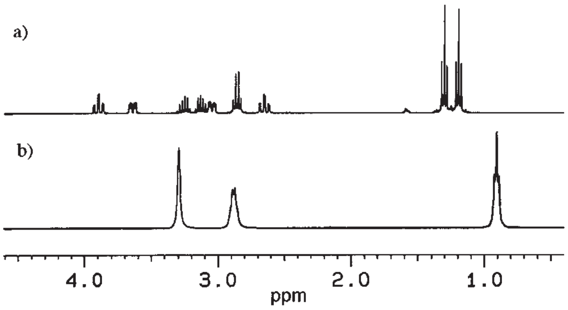
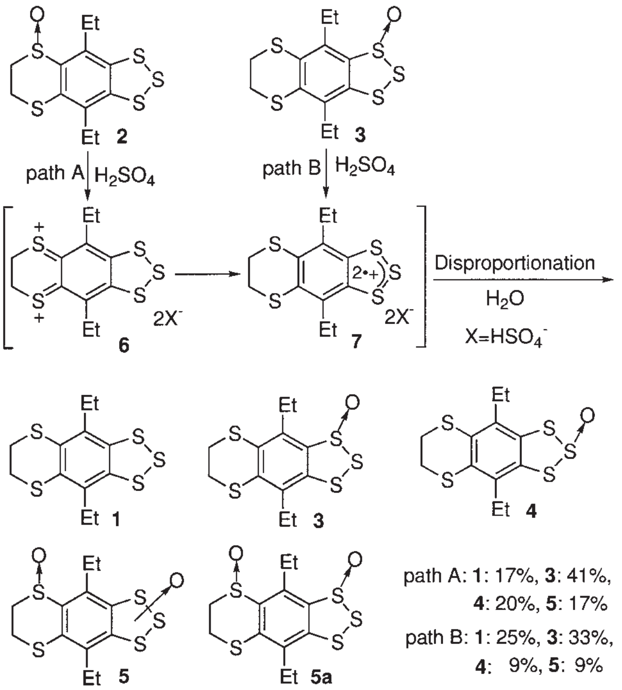


Figure 1. 400 MHz ^{1}H-NMR spectra of **2**: a) measured in $CDCl_3$; b) measured in D_2SO_4.

Subsequently, **3** was dissolved in D_2SO_4. In this case, the dark-purple color was not observed at all. So the dark-green colored solution generated was measured by ^{1}H-NMR; however, no signal was observed in the spectrum. Contrastively, when an H_2SO_4 solution of **3** was measured by ESR, one broadening signal was recorded similarly as mentioned above ($g = 2.017$). A treatment of **3** with H_2SO_4 and then with ice water gave **1** (25%), **3** (33%), **4** (9%), and **5** (9%) (Scheme 1). On the basis of these results, it appears that the dark-purple colored species, the dithia dication **6** was generated initially upon treatment of **2** with D_2SO_4 by way of the protonation and deoxygenation of sulfinyl oxygen; the positive charges generated on the dithiin ring consecutively transferred to the trithiole ring to produce the diradical dication **7**; the charge transfer should be accompanied by a change of the electronic state from singlet to triplet.[12]

Furthermore, the production of **1** and **5** by the hydrolysis of **6** and **7** is an important subject. Compounds **5** consisted of six disulfoxides, and the mixture was difficult to separate into each disulfoxide; however, only **5a** was isolated and the structure was determined by X-ray crystallography (Figure 2).[13,14] Since reduced product **1** and oxidized products **5** were produced by



Scheme 1. The compounds **5** consisted of six bissulfoxides, and only **5a** could be isolated as pure crystals.

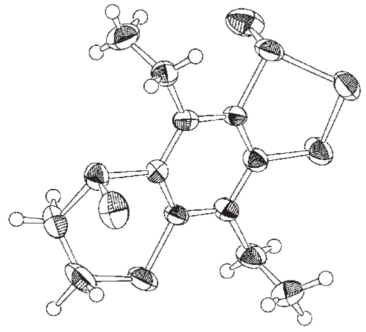


Figure 2. The ORTEP drawing of bissulfoxide **5a**.

treatment of **2** with H_2SO_4 and then with water, it is clear that a disproportionation of **7** proceeded successively in the H_2SO_4 solution. It was reported that the dispropotionation of a trithia dication proceeded in the H_2SO_4 solution to give corresponding sulfide and disulfoxide.[5] These results reveal that a mixture of a radical cation, a triradical trication, and a tetraradical tetracation derived from **7**, the dark-green colored species, should be generated as intermediates for the production of **1** and **5**, and the ESR signals were caused by those molecules.[15] Further investigation with respect to the species is now in progress.

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References and Notes

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8 Compound **1** (64 mg, 0.2 mmol) was treated with $NOPF_6$ (70 mg, 0.4 mmol) in CH_2Cl_2 (20 ml) and CH_3CN (1 ml) at −78 °C for 30 min and then with H_2O to give **3** and **4** in 70% (47 mg) and 13% (9 mg) yields, respectively, together with **1** in 14% recovery (9 mg); **3**: mp 140–141 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.27 (t, $J = 7.5$ Hz, 3H), 1.32 (t, $J = 7.5$ Hz, 3H), 3.01 (dq, $J = 14.4$, 7.5 Hz, 1H), 3.07 (dq, $J = 14.4$, 7.5 Hz, 1H), 3.11–3.37 (m, 6H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 12.4, 14.8, 28.2, 29.7, 29.9, 30.8, 132.3, 136.1, 138.3, 139.1, 141.2, 147.3; IR (KBr) 1074 cm^{-1} (SO); MS (m/z) 334 (M^+); Anal Found: C, 43.04; H, 4.20%. Calcd for $C_{12}H_{14}OS_5$: C, 43.08; H, 4.22%. **4**: mp 180–183 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.20 (t, $J = 7.5$ Hz, 6H), 2.94 (dq, $J = 14.2$, 7.5 Hz, 2H), 3.04 (dq, $J = 14.2$, 7.5 Hz, 2H), 3.10–3.33 (m, 4H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 13.0, 29.7, 30.9, 132.7, 134.2, 137.1; IR (KBr) 1116 cm^{-1} (SO); MS (m/z) 334 (M^+); Anal. Found: C, 43.07; H, 4.08%. Calcd for $C_{12}H_{14}OS_5$: C, 43.08; H, 4.22%.

9 The structure of **3** and **4** was determined by comparing their IR spectra with the references data; T. Kimura, M. Hanzawa, E. Horn, Y. Kawai, S. Ogawa, and R. Sato, *Tetrahedron Lett.*, **38**, 1607 (1997).

10 When **1** (321 mg, 1.0 mmol) was oxidized by *m*CPBA (196 mg, 1.0 mmol, assay ≥ 88%) in CH_2Cl_2 (100 ml), **2** was obtained in 67% (226 mg) yield together with **3** (25 mg, 7%), **4** (trace), and a mixture of six bissulfoxides **5** (trace), after purification by column chromatography (silica gel; CH_2Cl_2 and then CH_2Cl_2 : ethyl acetate = 1 : 1). The result suggests that the reactivity of the dithiin ring is higher than that of the trithiole ring in this oxidation reaction; **2**: mp 158.0–159.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.19 (t, $J = 7.5$ Hz, 3H), 1.30 (t, $J = 7.5$ Hz, 3H), 2.65 (ddd, $J = 13.8$, 13.8, 2.7 Hz, 1H), 2.68 (q, $J = 7.5$ Hz, 2H), 3.05 (ddd, $J = 13.8$, 4.7, 2.7 Hz, 1H), 3.14 (dq, $J = 15.0$, 7.5 Hz, 1H), 3.21 (dq, $J = 15.0$, 7.5 Hz, 1H), 3.64 (ddd, $J = 13.8$, 4.7, 2.7 Hz, 1H), 3.89 (ddd, $J = 13.8$, 13.8, 2.7 Hz, 1H); ^{13}C-NMR (101 MHz, $CDCl_3$) δ 11.9, 14.4, 15.1, 28.0, 28.7, 41.9, 131.3, 131.6, 135.5, 137.3, 140.6, 146.2; IR (KBr) 1020 cm^{-1} (SO); MS (m/z) 334 (M^+); Anal Found: C, 42.71; H, 4.44%. Calcd for $C_{12}H_{14}OS_5$: C, 43.08; H, 4.22%.

11 Compound **1** showed two reversible oxidation potentials at $E_{1/2} = 0.78$ and 1.12 V; T. Kimura, K. Tsujimura, S. Mizusawa, S. Ito, Y. Kawai, S. Ogawa, and R. Sato, *Tetrahedron Lett.*, **41**, 1801 (2000).

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13 **5a**: mp 180.5–182.5 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.30 (t, $J = 7.6$ Hz, 3H), 1.50 (t, $J = 7.5$ Hz, 3H), 2.70 (ddd, $J = 13.7$, 13.7, 2.6 Hz, 1H), 3.01 (q, $J = 7.6$ Hz, 2H), 3.14 (ddd, $J = 13.7$, 4.5, 2.6 Hz, 2H), 3.56 (dq, $J = 15.0$, 7.5 Hz, 1H), 3.64 (dq, $J = 15.0$, 7.5 Hz, 1H), 3.71 (ddd, $J = 13.7$, 4.5, 2.6 Hz, 1H), 3.96 (ddd, $J = 13.7$, 13.7, 2.6 Hz, 1H); IR (KBr) 1083, 1023 cm^{-1} (SO); MS (m/z) 350 (M^+); Anal Found: C, 41.11; H, 4.01%. Calcd for $C_{12}H_{14}O_2S_5$: C, 41.11; H, 4.03%.

14 The crystal data for **5a**: monoclinic, $P2_1/c$ (#14), $a = 8.7569(8)$ Å, $b = 9.569(2)$ Å, $c = 18.2457(8)$ Å, $\beta = 101.368(5)°$, $V = 1498.9(3)$ Å^3, $Z = 4$, $D_{calc} = 1.553$ g/cm^3, $\mu(\mathrm{CuK}\alpha) = 70.81$ cm^{-1}, 3118 reflections collected: 2920 unique reflection ($R_{int} = 0.051$), 2163 [$I > 1.50\sigma(I)$] used in the refinement, $R = 0.066$ ($Rw = 0.090$), $GOF = 1.02$; teXsan Structure Analysis Package, Molecular Structure Corp. (1985 and 1992); the oxygen atoms coordinated to the sulfur atoms are located on the axial position of the trithiole and dithiin rings, respectively.

15 Since the dispropotionation was not observed under the reaction of **1** with $NOPF_6$, it seems that **7** is stable at −78 °C.