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SYNTHESIS OF A NEW TYPE OF QUADRUPLY ORTHO-BRIDGED BIPHENYL COMPOUNDS WITH DISULFIDE LINKAGE, AND ITS SULFUR EXTRUSION IN CONCENTRATED H_2SO_4 AND PHOTOCHEMICAL CONDITION

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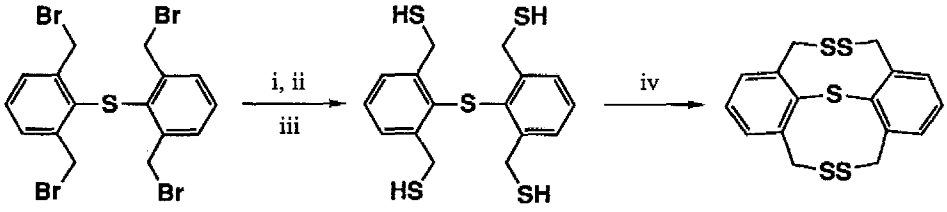
Abstract: A new methanodithiomethano-bridged dibenzotrithionin (**1**) has been synthesized. The electrochemical oxidation of **1** and its analogous compound was studied by cyclic voltammetry. A new type of the sulfur extrusion of **1** was found in the reaction of **1** with concd H_2SO_4 or 2 equiv of $NOPF_6$ and in its photochemical reaction.

Investigations of transannular interactions and reactions have provided numerous informations on the structures and reactivities of medium-sized cyclic compounds containing sulfur atoms.[1-3] Recently, we reported the transannular bond formation between the three sulfur atoms, i.e., dicationic salt of 1,11-(methanothiomethano)-5H,7H-dibenzo[b,g][1,5]dithiocin (**6**).[2] Furthermore, we found a new type of transannular pπ-(S^+-S^+) interaction in the reaction of 1,11-(etheno)-5H,7H-dibenzo[b,g][1,5]dithiocin (**8**) with concd H_2SO_4 or 2 equiv of $NOPF_6$.[3] These analogous compounds exhibit interesting physical and chemical properties on account of their unique arrangement of aromatic rings and heteroatoms in space. We now report the synthesis and characterization of a new methanodithiomethano-bridged dibenzotrithionin (**1**), and its unusual sulfur extrusion via the transannular S-S bond formation, and the photochemical reaction of 1 and related compounds with $(MeO)_3P$.

The title compound **1** was synthesized as follows (Scheme 1). Bis[2,6-bis(mercaptomethyl)phenyl]sulfide (**4**) was obtained by treating bis[2,6-bis(bromomethyl)phenyl]sulfide (**3**)[2] with thiourea, NaOH and HCl, and was purified by silica-gel column chromatography using n-hexane as eluant. A colorless crystal **4** was obtained in 74% yield.[4] Solutions of the tetrathiol **4** (950 mg, 2.56 mmol) in chloroform (100 mL) and iodine (1.56 g, 6.14 mmol) in chloroform (100 mL) were added separately and simultaneously over 1 h to a vigorously stirred solution of triethylamine (620 mg, 6.14 mmol) in chloroform (100 mL). After usual work-up, the crude product was purified on silica-gel column chromatography (eluant: n-hexane/$CHCl_3$) to give the compound **1** as colorless crystals, in 76% yield.[5]

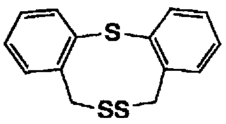


3 **4** **1**

Scheme 1. i, $(NH_2)_2CS$; ii, NaOH; iii, HCl; iv, I_2.

The compound **2** was prepared by the same method as **1**.[6]

The mass spectrum (EI) of **1** showed the molecular ion (M^+) at m/z 366. Other abundant fragments (m/z 334, 302, 270, 238, and 206) can be rationally explained in terms of loss of sulfur atoms from the molecular ion. Interestingly, the 500-MHz ^1H NMR spectrum of **1** in $CDCl_3$ at 25 °C showed that the signals assigned to the methylene hydrogens appeared as two sets of distinct AB quartet at δ 3.46 and 4.33 (ABq, J=15 Hz, 4H), 3.64 and 5.68 (ABq, J=15 Hz, 4H), indicating the rigid conformation in nine-membered ring with disulfide linkage. In contrast, the absorption of methylene protons of **2** in $CDCl_3$ at 25°C in its ^1H NMR appeared at δ 4.42 as broad singlet which can be assigned to the flexible conformers. In the UV spectra of compounds **1** and **2**, the compound **2** has a peak at λmax 240 nm (ε=9.90 X 10^3), while the bis-disulfide **1** has one at λmax 243 nm (ε=1.68 X 10^4) and another at 332 nm (ε=3.31 X 10^3).

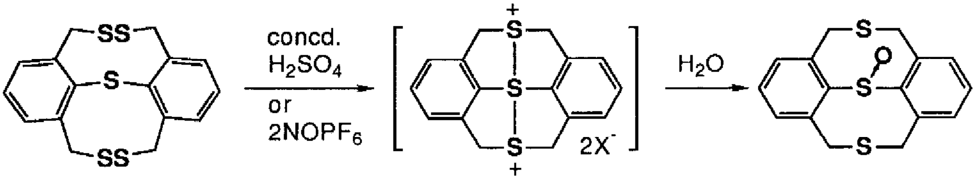


2

The electrochemical oxidations of bis-disulfide **1** and **2** were studied by cyclic voltammetry. Peak potentials of the first oxidation peak were determined at a glassy carbon working electrode (100 mV/s scan rate) in dichloromethane - 0.1M n-Bu_4NClO_4 vs Ag/0.01M $AgNO_3$ as reference electrode. The peak potentials (Ep) for **1** and **2** showed the following values: **1**, 1.16 V and **2**, 1.53 V. These oxidations were irreversible. Comparison of **1** with **2** shows a peak potential 370 mV more cathodic for the former, indicating that **1** is oxidized more readily. This facile oxidation of **1** can be explained by the intramolecular sulfur-sulfur interaction.[7]

The disulfide **2** did not change in concd H_2SO_4 as evidenced by ^1H NMR, and actually **2** was recovered. Surprisingly, when bis-disulfide **1** was dissolved in concd H_2SO_4, the monosulfoxide **5** was obtained in 48% yield after the hydrolysis of the H_2SO_4 solution of **1** (Scheme 2). Furthermore, the reaction of **1** with 2 equiv of $NOPF_6$, a one-electron-oxidizing agent, in

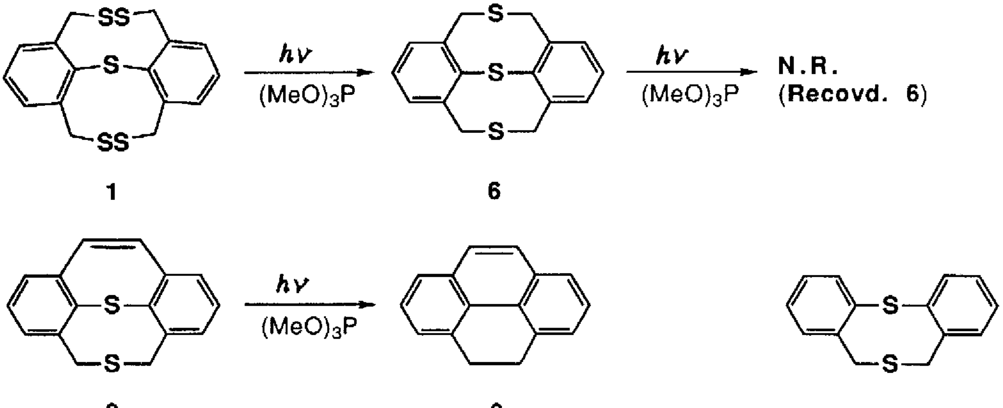
CH_3CN gave the solid, which on treatment with H_2O again resulted in the formation of the sulfoxide **5** (47%). Although we have no rational explanation for this reaction mechanism, one plausible mechanism can be proposed as follows. The reaction of **1** with concd H_2SO_4 or $NOPF_6$ (2 equiv) may proceed via the intermediary formation of the dication such as **7** with the extrusion of the two sulfur atoms by an electron-transfer reaction, since the sulfoxide **5** was also obtained by the hydrolysis of the stable dication **7** which was formed in the reaction of tris-sulfide **6** with concd H_2SO_4 or $NOPF_6$ (2 equiv).[2] These results indicate that the electrochemical study of **1** and **2** is consistent with the chemical data obtained by the reaction of **1** and **2** with concd H_2SO_4.



1 **7** **5**

Scheme 2

The photochemical reaction of the cyclic compounds containing polysulfur atoms, (**1**, **2**, **6**, **8**, and **10**) in the presence of trimethyl phosphite was studied (Scheme 3). Irradiation of bis-disulfide **1** in trimethyl phosphite at 15 °C using 400W high-pressure mercury lamp for 25 h gave the tris-sulfide **6** (82%) as a sole product by extrusion of the sulfur atoms. When the tris-sulfide **6** was further irradiated in trimethyl phosphite, **6** was recovered quantitatively.[8] Thus, the tris-sulfide **6** is inert toward photochemical



1 **6**

8 **9** **10**

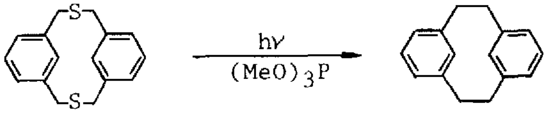
Scheme 3

reaction with $(MeO)_3P$, suggesting that the eight-membered ring of **6** is remarkably stabilized. On the other hand, the photolytic sulfur extrusion of etheno-bridged dibenzodithiocin **8**[3] in $(MeO)_3P$ afforded the dihydropyrene (**9**) in 91% yield. In contrast, the photochemical reaction of the compounds (**2** and **10**) with $(MeO)_3P$ gave the complex mixtures which could not be characterized. Thus, we observed the distinct difference of the reactivity in photochemical reaction of these polysulfur compounds with $(MeO)_3P$.

The results described herein indicate the intriguing reactivity and property of a new type of quadruply ortho-bridged biphenyl compounds with polysulfur atoms.

References and Notes

1) (a) K. Ohkata, K. Okada, and K. Akiba, Tetrahedron Lett., **26**, 4491 (1985).
   (b) K. Ohkata, K. Okada, K. Maruyama, and K. Akiba, Tetrahedron Lett., **27**, 3257 (1986).
   (c) K. Akiba, K. Takee, Y. Shimizu, and K. Ohkata, J. Am. Chem. Soc., **108**, 6320 (1986).
2) H. Fujihara, J.-J. Chiu, and N. Furukawa, J. Am. Chem. Soc., **110**, 1280 (1988).
3) H. Fujihara, J.-J. Chiu, and N. Furukawa, Tetrahedron Lett., **30**, 2805 (1989).
4) **4**: Mp 144-145 °C; FT-IR (KBr) 2567 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.66 (t, 4H), 3.83 (d, 8H), and 7.29 (br s, 6H). Anal. Calcd for $C_{16}H_{18}S_5$: C, 51.85; H, 4.90%. Found: C, 51.41; H, 4.81%.
5) **1**: Mp 265-266 °C; ^1H NMR (500-MHz, $CDCl_3$) δ 3.46 and 4.33 (ABq, J=15 Hz, 4H), 3.64 and 5.68 (ABq, J=15 Hz, 4H), 7.00 (d, 2H), 7.21 (t, 2H), and 7.26 (d, 2H); ^{13}C NMR (125-MHz, $CDCl_3$) δ 40.8, 45.1, 129.2, 129.5, 130.7, 131.6, 138.8, and 144.5; MS (m/z) 366 (M^+). Anal. Calcd for $C_{16}H_{14}S_5$: C, 52.42; H, 3.85%. Found: C, 52.26; H, 3.87%.
6) **2**: Mp 119-120 °C; ^1H NMR ($CDCl_3$) δ 4.42 (br s, 4H), 7.07-7.33 (m, 6H), and 7.53-7.82 (m, 2H). Anal. Calcd for $C_{14}H_{12}S_3$: C, 60.83; H, 4.38%. Found: C, 60.51; H, 4.35%.
7) For review: R. S. Glass, M. Hojjatie, A. Petsom, G. S. Wilson, M. Göbl, S. Mahling, and K.-D. Asmus, Phosphorus and Sulfur, **23**, 143 (1985).
8) Dithia[3.3]metacyclophane was easily converted to [2.2]metacyclophane upon irradiation with $(MeO)_3P$ as shown below: V. Boekelheide, I. D. Reingold, and M. Tuttle, J. Chem. Soc. Chem. Commun., 406 (1973).



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