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Synthesis and Structure of Novel Disulfide(trisulfide)-Containing Thiophenes

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Abstract: A novel trisulfide-containing thiophene, 1,5-dihydrothieno[3,4-*e*][1,2,3]-trithiepine (**5**), and a disulfide analogue, 1,4-dihydrothieno[3,4-*d*][1,2]dithiine (**4**), were designed and synthesized. All the compounds were characterized by FT-IR, NMR, Raman, MS, and elemental analysis, some of which were confirmed by single-crystal structure analysis. The designed molecules have potential usage as the cathode material for batteries.

Keywords: alkylbromination, disulfide, methylation, thioesterification, thiophene, trisulfide

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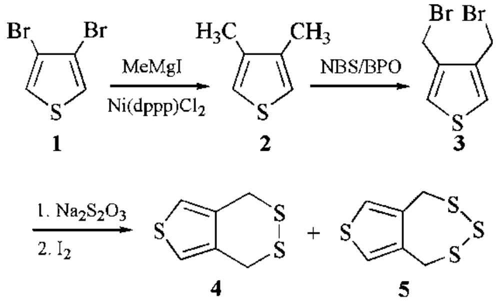
Organodisulfide compounds have been introducted as a new organic cathode material in lithium batteries because of their high specific energy.[1] A series of compounds[2,3] having S-S groups within the molecules are being considered as energy storage materials, whereby energy exchange occurs based on the reversible polymerization–depolymerization process (2SH ↔ S-S). At the same time, polythiophene (PTh) and its derivatives[4] have been investigated intensely because of their interesting electrical and electronic properties and relatively good environmental stability, which makes them good candidates for the cathode material of lithium secondary batteries.[5] According to our previous studies and related references,[6–8] when a six-membered cycle containing S-S bond was introduced as an electrode material into the backbone of some kind of conducting polymer, the compound was expected to have some excellent behaviors, such as enhanced redox process and prolonged cyclic life.

For this article, we designed, synthesized, and characterized a new trisulfide-containing thiophene derivative and a disulfide analogue, both with a condensed aliphatic ring containing a trisulfide(disulfide) bond at the 3,4-position of thiophene ring. Its high disulfide density and intramolecular S-S bonds can lead to high effectivity as a potential battery material.[6]

The total synthesis for target compounds 1,4-dihydrothieno[3,4-*d*][1,2]dithiine (**4**) and 1,5-dihydrothieno[3,4-*e*][1,2,3]trithiepine (**5**) is achieved in three steps starting from 3,4-dibromo-thiophene (**1**) as outlined in Scheme 1. First, the starting material **1** was converted to 3,4-dimethyl-thiophene(**2**) in 88% yield, which was modified from Tamao's Grignard coupling reaction.[9] In contrast, we gave up on our attempt to methylate **1** by n-butyllithium, followed by dimethylsulfate.[10] Although its reaction time was shorter than the Grignard's, the reaction conditions was too rigorous, especially its low temperature (−78°C). When it slightly raised to −70 to −60°C, some complicated by-products, such as 2,3,4-trimethyl-thiopene and 2,3,5-trimethyl-thiopene, would appear, which seriously lower the product's yield. These by-products can de determined by ^{1}H NMR analysis of the crude product.



Scheme 1. Synthesis of compound **4** and **5**.

The alkylate **2** was then brominated to 3,4-bis-bromomethyl-thiophene (**3**) by *N*-bromosuccinimide (NBS) in the presence of BPO (benzoyl peroxide) in 33% yield. This bromination reaction was only mentioned in the literature,[11] without detailed description.

Finally, the bromide **3** was converted to target molecules **4** and **5**. This process was accomplished via two steps. First, an intermediate (sodium alkylthiosulfate) was yielded by reaction of compound **3** and $Na_2S_2O_3$, and the intermediate was then directly converted to disulfide and trisulfide by the oxidation of I_2, without any purification. Sodium alkylthiosulfate[12–14] (Bunte salts) has been reported as a generally used reagent to form a disulfide compound by reaction with iodine or hydrogen peroxide. In this case, we completed the reaction with iodine, but hydrogen peroxide did not work. Furthermore, not only disulfide but also trisulfide was synthesized in one pot, which has not been reported in the literature under similar reaction circumstances.

Both of the target compounds were characterized by ^1H NMR analysis. It is noteworthy that the spectrum of disulfide **4** shows all four methylene protons to be equivalent, by virtue of rapid conformational interchange. In contrast, the four methylene protons of the larger trisulfide ring in the trithiepine (**5**) appeared as an AB quartet, indicating a higher degree of rigidity of the conformational isomers. Its NMR signals were similar to other trisulfide-containing molecules.[15]

Raman spectroscopy has always been a powerful research tool to characterize sulfur-rich compounds, because they give very intense Raman spectra because the valence electrons in S-S bonds are highly polarizable.[16] In this work, the S-S stretching vibrations of compounds **4** and **5** in Raman spectra were observed at 503 and 478 cm^{-1} respectively.

We successfully grew single crystals of compounds **3**, **4**, and **5** from $CHCl_3/C_2H_5OH$ and submitted them to X-ray crystallography. Their single-crystal analysis data confirmed their molecular structures. The ORTEP drawing of the three compounds are shown in Figs. 1–3, respectively.

In conclusion, a three-step synthesis in 18% total yield of a novel trisulfide-containing thiophene, 1,5-dihydrothieno[3,4-*e*][1,2,3]trithiepine (**5**), and a disulfide analogue, 1,4-dihydrothieno[3,4-*d*][1,2]dithiine (**4**), have been developed. During the synthesis of target compounds, Grignard coupling reaction accomplished the methylation instead of n-butyllithium and dimethylsulfate, to ensure the purity and conversion yield. Furthermore, we synthesized trisulfide and disulfide compounds in one pot through an intermediate (Bunte salts), which has not been reported in relevant literature. The single-crystal structures of three compounds, **3**, **4**, and **5**, were reported. When the designed molecule is polymerized, it has potential to be used as the cathode material of secondary lithium batteries. The corresponding research work on polymerization is under way.

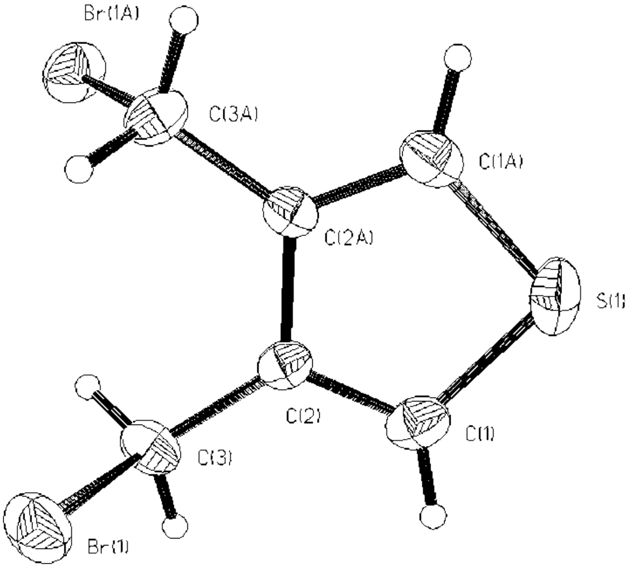


Figure 1. ORTEP drawing of the molecular structure of **3**, CCDC reference number 256418.

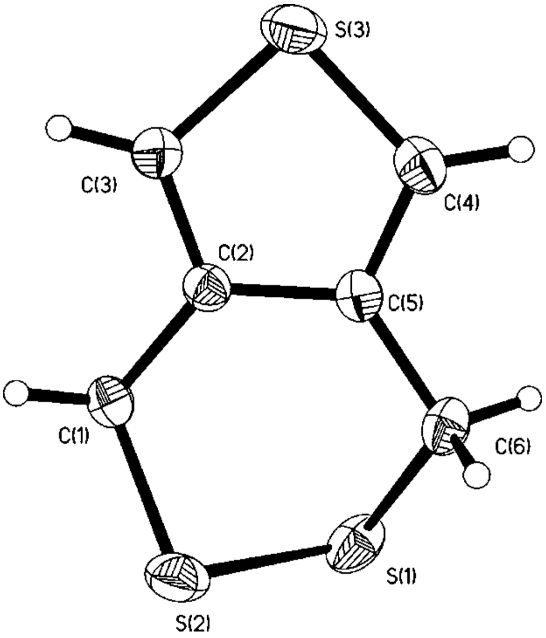


Figure 2. ORTEP drawing of the molecular structure of **4**, CCDC reference number 267119.

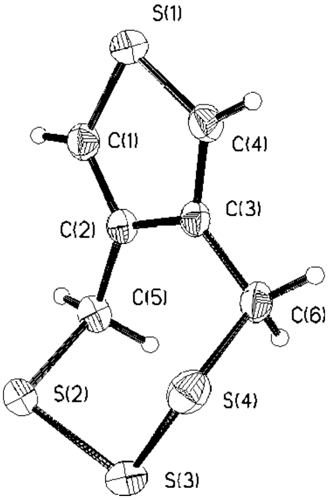


Figure 3. ORTEP drawing of the molecular structure of **5**, CCDC reference number 264691.

EXPERIMENTAL SECTION

General

3,4-Dibromo-thiophene (**1**) was purified under reduced-pressure distillation; N-bromosuccinimide (NBS) was recrystallized from H_2O. Other commercially available reagents were used without further purification, unless otherwise noted. All solvents used for extractions or reactions were dried according to standard procedures and kept over molecular sieves. Dichloro[1,3-bis(diphenylpgosphino)propane]nickel[17] (Ni(dppp)Cl_2) and methylmagnesium iodide[18] (MeMgI) were prepared according to literature procedures.

Melting points were taken on a micro-melting apparatus and are uncorrected. NMR spectra were obtained on Varian Mercury-VX 300 spectrometers. Spectra were recorded in $CDCl_3$, using TMS as internal standard at 300 MHz for ^1H and 125 Hz for ^{13}C at 298 K if not stated otherwise; δ values are given in parts per million (ppm), and coupling constants are reported in Hertz. FT-IR spectra were recorded on a Shimadzu infrared spectrophotometer (values in centimeters^{-1}). Raman spectra were recorded on a Nexus 670 spectrophotometer. Mass spectra were obtained on a Thermo Finnigan Trace MS Plus. The elemental analyses were measured with a Finnigan Flash 1112 Series EA. The crystal data were collected with a Bruker AXS Smart 1000 CCD. Chromatographic separations were performed using silica gel 60 (200–300 mesh).

3,4-Dimethyl-thiophene (2)

3,4-Dibromo-thiophene (**1**) (10.4 g, 43.0 mmol) and [(Ni(dppp)Cl_2)] (0.15 g 0.3 mmol) was dissolved in 70 mL of dry ether then the above mixture was dropped into a solution of methylmagnesium iodide (17.0 g, 102 mmol) in 70 mL of ether at 0°C under an N_2 atmosphere for 30 min. After the addition, the mixture was refluxed for 20 h. The resulting mixture was treated with 50 mL of HCl (2 N) in an ice bath to remove the excess MeMgI, and the organic layer was then washed with H_2O (2 × 70 mL) and dried over $MgSO_4$. Removal of the solvent gave a light yellow oil residue, which was purified using silica-gel chromatography (petroleum ether) to give 4.2 g (88%) of **2** as a yellow odorous oil: bp 143–144°C (lit.[10] bp 144°C); ^{1}H NMR ($CDCl_3$) δ 6.88 (s, 2H, α-H), 2.16 (s, 6H, Ar-CH_3); FT-IR (neat) 3090 ($\nu_{\text{Ar-H}}$), 2922, 2860, 1444 ($\nu_{\text{C-H}}$) cm^{-1}.

3,4-bis-Bromomethyl-thiophene (3)[11]

The compound **2** (3.0 g, 26.7 mmol), N-bromosuccinimide (9.5 g, 53.4 mol), and benzoyl peroxide (0.25 g, 1 mmol) were refluxed in 120 mL of CCl_4 for 5 h. After the mixture was filtered, the succinimide was washed with CCl_4 (2 × 10 mL). Then the organic solution was combined and concentrated under reduced pressure. The red-brown oil thus obtained was crystallized from CCl_4 to give 2.4 g (33%) of white crystals: mp 83–84 °C; ^{1}H NMR ($CDCl_3$) δ 7.35 (s, 2H, s, 2H, α-H), 4.63 (s, 4H, Ar-CH_2); FT-IR(KBr) 3091, 3028 (ν $_{\text{Ar-H}}$), 2924, 1422 (ν $_{\text{C-H}}$) cm^{-1}.

1,4-Dihydrothieno[3,4-*d*][1,2]dithiine (4) and 1,5-Dihydrothieno[3,4-*e*][1,2,3]trithiepine (5)

The compound **3** (2.7 g, 10.0 mmol) and sodium thiosulphate (4.96 g, 20.0 mmol) were dissolved in 80 mL of EtOH/H_2O (1 : 1). The mixture was refluxed with stirring until the solution was homogeneous. The iodine was then added in small portions until the color remained. Then a sodium bisulfite solution was added to remove the excess iodine. After filtration, the brown-black precipitation was extracted by 100 mL of boiling $CHCl_3$; then the organic solution was washed with water (2 × 50 mL) and dried over $MgSO_4$. Evaporation of the solvent left a yellow solid residue, which was purified using silica-gel chromatography (petroleum ether/chloroform 10:3) to give 0.66 g (38%) of **4** and 0.50 g (24%) of **5**.

Compound **4** was a white solid: mp 91–92°C (lit.[19] 92–93°C); ^{1}H NMR ($CDCl_3$) δ 7.03 (s, 2H, α-H), 4.05 (s, 4H, Ar-CH_2); ^{13}C NMR ($CDCl_3$) δ 132.1, 121.9, 33.4; FT-IR (KBr) 3077, 2897, 1363, 1229 cm^{-1}; Raman 503 (ν $_{\text{S-S}}$)

cm^{-1}; MS(EI) 174[M]$^+$; anal. for $C_6H_6S_3$ calcd.: C, 41.34; H, 3.47; S, 55.19, Found: C, 41.56; H, 3.52; S, 54.92.

Compound **5** was a white solid: mp 105–106°C; ^{1}H NMR ($CDCl_3$) δ 7.07 (s, 2H, α-H), 4.36 (AB pattern, $\Delta\delta = 0.12$ ppm, $J = 15$ Hz, 4H, Ar-CH_2); ^{13}C NMR ($CDCl_3$) δ 141.0, 125.3, 44.3; FT-IR (KBr) 3074, 2924, 1399, 1226 cm^{-1}; Raman 478($\nu_{S\text{-}S}$) cm^{-1}; MS(EI) 206[M]$^+$; anal. for $C_6H_6S_4$ calcd: C, 34.92; H, 2.93; S, 62.15. Found: C, 34.98; H, 3.02; S, 62.04.

X-Ray Crystallographic Data

The crystal structures of compounds **3**, **4**, and **5** were determined, using data collected at 293 K with Mo K_α radiation on a Bruker AXS CCD diffractometer. The structures were solved by direct methods (SHELXS-97) and refined using full-matrix least-squares on F^2.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the reference numbers CCDC 256418, CCDC 267119, and CCDC 264691. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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REFERENCES

1. Liu, M.; Visco, S. J.; De Jonghe, L. C. Electrode kinetics of organodisulfide cathodes for storage batteries. *J. Electrochem. Soc.* **1990**, *137*, 750–759.
2. Oyama, N.; Tatsumi, T.; Sato, T.; Sotomura, T. Dimercaptan–polyaniline composite electrodes for lithium batteries with high energy density. *Nature* **1995**, *373*, 598–600.
3. Naoi, K.; Kawase, K.; Mori, M.; Komiyama, M. Electrochemistry of poly(2,2′-dithiodianiline): A new class of high energy conducting polymer interconnected with S-S bonds. *J. Electrochem. Soc.* **1997**, *144*, L173–L175.
4. Roncali, J. Conjugated poly(thiophenes): Synthesis, functionalization, and applications. *Chem. Rev.* **1992**, *92*, 711–738.
5. Navák, P.; Müller, K.; Santhanam, K. S. V.; Haas, O. Electrochemically active polymers for rechargeable batteries. *Chem. Rev.* **1997**, *97*, 207.
6. Deng, S.-R.; Kong, L.-B.; Hu, G.-Q.; Wu, T.; Li, D.; Zhou, Y.-H.; Li, Z.-Y. Benzene-based polyorganodisulfide cathode materials for secondary lithium batteries. *Electrochim. Acta* **2006**, *51*, 2589–2593.

7. Li, J.-X.; Zhan, H.; Zhou, L.; Deng, S.-R.; Li, Z.-Y.; Zhou, Y.-H. Aniline-based polyorganodisulfide redox system of high energy for secondary lithium batteries. *Electrochem. Commun.* **2004**, *6*, 515–519.
8. Cho, J. S.; Sato, S.; Takeoka, S.; Tsuchida, E. Synthesis of disulfide-containing aniline and copolymerization with aniline. *Macromolecules* **2001**, *34*, 2751–2756.
9. Tamao, K.; Kodama, I.; Kumada, M.; Minato, A.; Suzuki, K. Nickel–phosphine complex–catalyzed Grignard coupling, II. *Tetrahedron* **1982**, *38*, 3347–3354.
10. Janda, M.; Srogl, J.; Stibor, I.; Nemec, M.; Vopatrna, P. Polylithiothiophenes and a convenient synthesis of polymethylthiophenes. *Synthesis* **1972**, *10*, 545–547.
11. Hanack, M.; Schmid, U.; Roehrig, U.; Toussaint, J. M.; Adant, C.; Bredas, J. L. 1,3-Bis(2-thienylmethylene)-1H,3H-thieno[3,4-c]thiophene: A precursor for a new low-band-gap polymer. *Chem. Ber.* **1993**, *126*, 1487–1491.
12. Westlake, H. E.; Dougherty, G. The use of Buntes salts in eynthesis, III: The preparation of aliphatic disulfides. *J. Am. Chem. Soc.* **1942**, *64*, 149–150.
13. Deng, S.-R.; Wu, L.; Wang, H.; Zhou, B.; Li, Z.-Y.; Zhou, Y.-H.; Wong, W.-K.; Guo, J.-P. Synthesis and structure of a novel disulfide-containing aniline. *Synth. Commun.* **2005**, *35*, 129–135.
14. Deng, S.-R.; Hu, G.-Q.; Yan, Y.; Guo, J.-P.; Huang, W.-G.; Zhou, Y.-H.; Li, Z.-Y. A new synthetic route of disulfide containing aniline compounds. *Chin. J. Org. Chem.* **2005**, *25*, 815–818.
15. Harpp, D. N.; Smith, R. A.; Steliou, K. Studies toward cyclic trisulfides: Trisulfide polymers and sulfur extrusion. *J. Org. Chem.* **1981**, *46*, 2072–2079.
16. Steudel, R. The chemistry of organic polysulfanes R-S_n-R ($n > 2$). *Chem. Rev.* **2002**, *102*, 3905–3945.
17. Van Hecke, G. R.; Horrocks, W. D. W., Jr. Ditertiary phosphine complexes of nickel: Spectral, magnetic, and proton resonance studies: A planar-tetrahedral equilibrium. *Inorg. Chem.* **1966**, *5*, 1968–1974.
18. Salinger, R. M.; Mosher, H. S. Infrared spectral studies of Grignard solutions. *J. Am. Chem. Soc.* **1964**, *86*, 1782–1786.
19. Hayakawa, K.; Wernet, W.; Takeshita, K.; Kang, W.-B. Polymerizable pyrroles and thiophenes used for electroconductive polymers and electrode active substances. Brit. UK Pat. Appl. 1995, GB 2288799.