



Pergamon

Tetrahedron Letters 41 (2000) 1801–1805

TETRAHEDRON
LETTERS

Photolytic preparation, structure, and electrochemical properties of thianthrene derivatives bearing trithiole and dithian rings

Takeshi Kimura,^a Kazuhiko Tsujimura,^a Susumu Mizusawa,^a Shinya Ito,^a Yasushi Kawai,^b Satoshi Ogawa^a and Ryu Sato^{a,*}

^a*Department of Applied Chemistry and Molecular Science, Faculty of Engineering, Iwate University, Morioka 020-8551, Japan*

^b*Institute for Chemical Research, Kyoto University, Uji 611-0011, Japan*

Received 8 November 1999; revised 22 December 1999; accepted 24 December 1999

Abstract

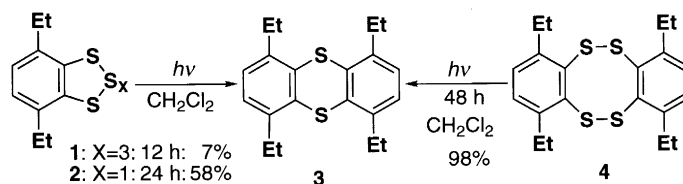
Photolytic desulfurization and ring-contraction reactions of diethyl benzotrithiole and tetraethyl dibenzotetrathiocin proceeded without a desulfurization reagent such as trialkyl phosphite by irradiation with a 100 W high-pressure Hg lamp in CH₂Cl₂ under Ar to produce tetraethyl thianthrene. By means of the photolysis, the thianthrene derivatives bearing trithiole and dithian rings on both sides of thianthrene were obtained in good yields. © 2000 Elsevier Science Ltd. All rights reserved.

The chemistry of cyclic polysulfides has become of great interest to organic sulfur chemists with respect to the synthesis, structure, reactivities, and electrochemical properties.^{1,2} On the other hand, a photolytic sulfur extrusion reaction of cyclic sulfides has been known as common methodology for the preparation of strained molecules and cyclophanes; however, trialkyl phosphite which was used as a solvent and a desulfurization reagent was essential to the photolytic reaction.^{3,4} On the photolysis of diethyl benzotrithiole (**2**) and 1,4,7,10-tetraethyl dibenzo[*c,g*][1,2,5,6]tetrathiocin (**4**), desulfurization and ring-contraction reactions proceeded without trialkyl phosphite to produce tetraethyl thianthrene (**3**).⁵ Since the reaction was free from a desulfurization reagent, it was possible to apply the photolysis to the double polysulfide ring system, 4,8-diethyl benzo[1,2-*d*;4,5-*d'*]bis[1,2,3]trithiole (**5**) and 4,9-diethyl [1,4]dithiano[6,5-*f*]benzotrithiole (**9**). In order to prepare new thianthrene derivatives bearing two cyclic polysulfide rings, photolysis of **5** and **9** was performed to give the corresponding thianthrenes in good yields. This paper reports the results of novel photolytic reactions of benzotrithioles and dibenzotetrathiocins producing several thianthrene derivatives.

Unsubstituted benzopentathiepin was unstable in light and decomposed gradually to produce unidentified products. To verify the photolytic reaction of diethyl benzopentathiepin, **1** (44 mg, 0.15 mmol) was irradiated with a 100 W high-pressure Hg lamp in CH₂Cl₂ (23 ml) under Ar for 12 h to produce **3** in 7%

* Corresponding author. E-mail: rsato@iwate-u.ac.jp (R. Sato)

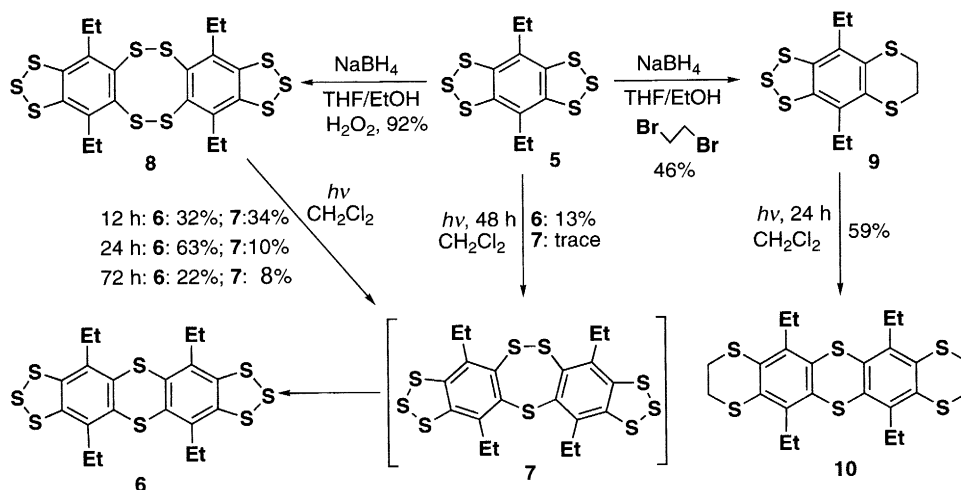
yield together with **2** in 31% yield (Scheme 1).⁶ The photolysis of **2** (102 mg, 0.45 mmol, in 68 ml of CH₂Cl₂) for 24 h gave **3** in 58% yield together with the recovery of **2** (31%).



Scheme 1.

The photolysis of **1** and **2** proceeded via consecutive desulfurization, dimerization, and ring-contraction reactions. As an intermediate, a dimerized compound such as **4** should be generated initially in the photolytic reaction. Recently, we have reported that the photolysis of 1,4,7,10-tetraisopropyl dibenzo[*c,g*][1,2,5,6]tetrathiocin gave the corresponding thianthrene in quantitative yield.⁷ Therefore, **4** was prepared from 4,7-diethyl-2,2-dimethyl benzo[1,3,2]dithiastannole,⁸ and was photolyzed under Ar for 48 h (**4**: 22 mg, 0.06 mmol, in 20 ml of CH₂Cl₂) to produce **3** in 98% yield.

These results prompted us to apply the photolytic reaction to **5** and **9** bearing the trithiole and dithian rings on both sides of the benzene ring. On the photolysis of **5** (37 mg, 0.11 mmol, in 15 ml of CH₂Cl₂) for 48 h, 4,6,10,12-tetraethyl bis(trithiolo)[*b,i*]thianthrene (**6**) was obtained in 13% yield together with a trace amount of dibenzotrithiepin derivative **7** (Scheme 2).⁹ Although **5** was photolyzed under several photolytic reaction conditions, the yield of **6** was not increased and unidentified products were obtained mainly on prolonging the reaction time. In the UV spectra, the absorption wavelength of **6** is similar to that of **5** (Table 1). It appeared that **6**, obtained by the photolysis, decomposed and was further desulfurized under the reaction conditions. Meanwhile, when **9** (32 mg, 0.1 mmol, in 15 ml of CH₂Cl₂) was photolyzed for 24 h, 1,4,6,9-tetraethyl-2,3,7,8-bis(ethylenedithio)thianthrene (**10**) was obtained in 59% yield as colorless crystals together with the recovery of **9** (22%).¹⁰ The compound **10** was stable compared with **6** under the photolytic reaction conditions.



Scheme 2.

In order to demonstrate that **6** is not bis(tetrathiano)biphenylene but bis(trithiolo)thianthrene, X-ray crystallographic analysis of **6** was performed (Fig. 1).¹¹ The ORTEP drawing reveals that **6** is bis(trithiolo)thianthrene bearing two trithiole rings on both sides of thianthrene. The bond lengths and

Table 1
Redox potentials and UV spectra

Compounds	E1/2 (V)		UV λ_{\max} nm (ϵ)	
1			299 (3600)	355 (1200, sh)
2^a	0.71		274 (7100)	325 (1500)
3^a	0.89		261 (28000)	295 (4300)
4			317 (7500)	350 (2500, sh)
5^b	0.83	0.95	297 (17000)	353 (2500)
6^b	0.88 ^d		294 (37000)	341 (6200)
8			300 (36000)	361 (12000)
9^c	0.78	1.12	288 (18000)	341 (2800, sh)
10^c	0.80	1.02	282 (68000)	313 (11000, sh) 326 (7500, sh)

The redox potentials were determined by cyclic voltammetry using Ag/0.01 M AgNO₃ as a reference electrode; ^aMeasured in CH₃CN; ^bMeasured in CH₂Cl₂:CH₃CN=1:1; ^cMeasured in CH₂Cl₂; ^dQuasi reversible (Ep V); Scan rate: 200 mV/s. The UV spectra were measured in CH₂Cl₂.

bond angles of the trithiole and central dithiin rings of **6** are similar to those of the benzotrithioles and thianthrenes reported.^{1,12} Therefore, **6** is expected to have related reactivity and electrochemical property to those of benzotrithiole and thianthrene.

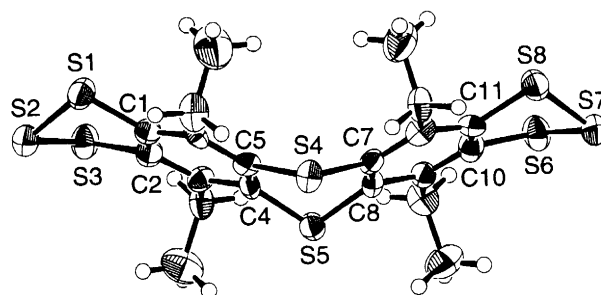


Fig. 1. The ORTEP drawing of **6**

To exploit the ring-contraction reaction of dibenzotetrathiocin to the preparation of **6**, the compound **8** was prepared in 92% yield by treatment of **5** (323 mg, 1.0 mmol, in 20 ml of THF and 5 ml of EtOH) with NaBH₄ (38 mg, 1.0 mmol) and then H₂O₂ (0.1 ml, 1.0 mmol) for dimerization (Scheme 2).¹³ As shown in Table 1, **8** has higher absorptivity than **5** and **6** in the UV spectra although their absorption wavelengths exist in similar regions. Since **8** has a low solubility in organic solvents at room temperature, a suspended solution of **8** (291 mg, 0.5 mmol, in 200 ml of CH₂Cl₂, under Ar) was photolyzed under several reaction conditions to give **6** and **7**, and irradiation for 24 h gave the best results; 12 h: **6** (32%), **7** (34%); 24 h: **6** (63%), **7** (10%); 72 h: **6** (22%), **7** (8%).¹⁴ These results reveal that the photolytic reaction of **8** proceeded faster than that of **5** and **6** under the reaction conditions, and **7** was generated initially in the photolysis of **8** and was further desulfurized to give **6**. On the other hand, **7** was unstable and decomposed slowly to produce **6** and elemental sulfur.¹⁵ To determine the reaction pathway, the photolysis of **7** was monitored by ¹H NMR. As shown in Fig. 2, a 1:1 mixture of **6** and **7** was prepared by the photolysis of **8** (Fig. 2a), and was photolyzed in CDCl₃. After 24 h, the signal of **7** disappeared (Fig. 2b), suggesting that **7** and **8** should be intermediates in the photolysis of **5**.¹⁶ Meanwhile, trace amounts of 6,10-diethyl trithiolo[*h*]benzopentathiepin and **5** were produced as minor products on the photolysis of **8** via cleavage

of two central disulfide bonds and consecutive sulfurization and cyclization reactions with sulfur atoms generated in the reaction.

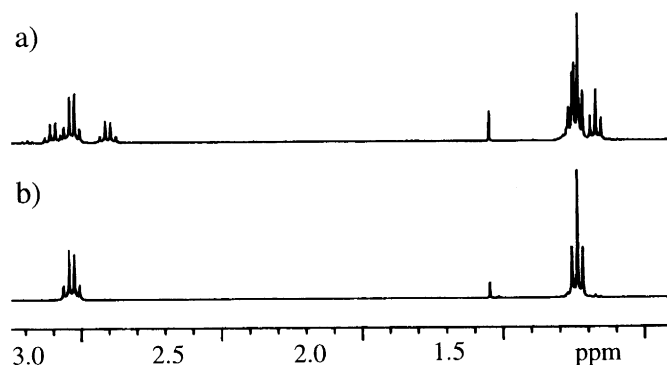


Fig. 2. 400 MHz ^1H NMR spectra; (a) a 1:1 mixture of **6** and **7** in CDCl_3 ; (b) after irradiation for 24 h, **7** was consumed

It is worthwhile to examine redox potentials of thianthrene and benzotrithiole derivatives, to determine their electrochemical properties (Table 1). The compounds **2** and **3** showed one reversible redox potential at $E_{1/2}=0.71$ V and $E_{1/2}=0.89$ V, respectively. Furthermore, two reversible redox potentials were recorded for **5** ($E_{1/2}=0.83, 0.95$ V), **9** ($E_{1/2}=0.78, 1.12$ V), and **10** ($E_{1/2}=0.80, 1.02$ V). Meanwhile, first and second redox potentials of **6** were in close proximity comparing with those of **5**, **9**, and **10**, and hence the cyclic voltammogram of **6** was observed as one quasi reversible peak. These results suggest that a multicentric redox system can be constructed in **6** and **10** between their trithiole and dithian rings through central thianthrene. Further investigation of this photolytic reaction is in progress in this laboratory.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas of the Chemistry of Inter-element Linkage (No. 11120205) from the Ministry of Education, Science, Sports and Culture of Japan.

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6. The compounds **1** and **2** were prepared from 4,7-diethyl-2,2-dimethyl benzo[1,3,2]dithiastannole in 60 and 30% yields by the method previously reported: Ogawa, S.; Yomoji, N.; Chida, S.; Sato, R. *Chem. Lett.* **1994**, 507; Ogawa, S.; Kikuchi, T.; Sasaki, A.; Chida, S.; Sato, R. *Tetrahedron Lett.* **1994**, 35, 5469. Compound **1**: mp 38.0–39.0°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.21 (t, $J=7.5$ Hz, 6H), 2.88 (dq, $J=13.8, 7.5$ Hz, 2H), 2.98 (dq, $J=13.7, 7.5$ Hz, 2H), 7.19 (s, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 16.4, 29.8, 131.5, 144.1, 147.9; MS (m/z) 292 (M^+); anal. calcd for $\text{C}_{10}\text{H}_{12}\text{S}_5$: C, 41.06; H, 4.13. Found: C, 41.21; H, 4.47; compound **2**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.21 (t, $J=7.5$ Hz, 6H), 2.68 (q, $J=7.5$ Hz, 4H), 6.89 (s, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 14.7, 30.3, 127.2, 138.1, 140.2; MS (m/z) 228 (M^+); anal. calcd for $\text{C}_{10}\text{H}_{12}\text{S}_3$: C, 52.29; H, 5.30. Found: C, 52.51; H, 5.39; compound **3**: mp 101.5–102.0°C (decomp); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.28 (t, $J=7.5$ Hz, 12H), 2.94 (q, $J=7.5$ Hz, 8H), 7.11 (s, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 15.3, 27.9, 127.3, 136.0, 141.5; MS (m/z) 328 (M^+); Anal. calcd for $\text{C}_{20}\text{H}_{24}\text{S}_2$: C, 73.12; H, 7.36. Found: C, 72.89; H, 7.54.
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8. The compound **4** was prepared in 60% yield by treatment of 4,7-diethyl-2,2-dimethyl benzo[1,3,2]dithiastannole with *n*-BuLi in THF under N_2 at 0°C and then with O_2 for dimerization at room temperature. Compound **4**: mp 209.0–210.0°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.27 (t, $J=7.5$ Hz, 12H), 2.98 (dq, $J=13.7, 7.5$ Hz, 4H), 3.04 (dq, $J=13.7, 7.5$ Hz, 4H), 7.24 (s, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 16.4, 29.7, 131.1, 142.1, 148.3; MS (m/z) 392 (M^+); anal. calcd for $\text{C}_{20}\text{H}_{24}\text{S}_4$: C, 61.18; H, 6.16. Found: C, 61.23; H, 5.96.
9. Compound **6**: mp 237–238°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.24 (t, $J=7.5$ Hz, 12H), 3.03 (q, $J=7.5$ Hz, 8H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 14.2, 30.5, 136.2, 137.2, 141.3; MS (m/z) 516 (M^+); anal. calcd for $\text{C}_{20}\text{H}_{20}\text{S}_8$: C, 46.47; H, 3.90. Found: C, 46.49; H, 3.99.
10. Compound **9**: mp 114–116°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.16 (t, $J=7.5$ Hz, 6H), 2.90 (d, $J=7.5$ Hz, 4H), 3.19 (s, 4H); MS (m/z) 318 (M^+); anal. calcd for $\text{C}_{12}\text{H}_{14}\text{S}_5$: C, 45.24; H, 4.43. Found: C, 45.29; H, 4.38; compound **10**: mp 239–242°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.23 (t, $J=7.5$ Hz, 12H), 3.17 (s, 8H), 3.23 (q, $J=7.5$ Hz, 8H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 14.2, 26.3, 31.0, 133.6, 134.1, 140.7; MS (m/z) 508 (M^+); anal. calcd for $\text{C}_{24}\text{H}_{28}\text{S}_6$: C, 56.65; H, 5.55. Found: C, 56.35; H, 5.34.
11. The crystal data of **6**: tetragonal: $\text{P}\bar{4}$ (#81), $a=23.545(1)$ Å, $c=4.824(2)$ Å, $V=2674.2(7)$ Å³, $Z=4$, $\mu(\text{CuK}\alpha)=62.1$ cm⁻¹, $D_c=1.28$ g/cm³, $R=0.062$ ($R_w=0.099$), $GOF=1.14$; teXsan Structure Analysis Package, Molecular Structure Corporation (1985 and 1992).
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13. Compound **8**: mp 239.5–241.5°C (decomp); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.24 (t, $J=7.5$ Hz, 12H), 3.06 (dq, $J=15.0, 7.5$ Hz, 4H), 3.13 (dq, $J=15.0, 7.5$ Hz, 4H); MS (m/z) 516 ($\text{M}^+ - 64$); anal. calcd for $\text{C}_{20}\text{H}_{20}\text{S}_{10}$: C, 41.34; H, 3.47. Found: C, 41.15; H, 3.60.
14. The yields of **6** and **7** were determined by the integral ratio of $^1\text{H NMR}$. Compound **7**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.17 (t, $J=7.6$ Hz, 6H), 1.25 (t, $J=7.6$ Hz, 6H), 2.91 (q, $J=7.6$ Hz, 4H), 3.10 (q, $J=7.6$ Hz, 4H).
15. Since **7** could not be isolated from **6**, a mixture of **6** and **7** was treated with excess amounts of NaBH_4 and then MeI in THF/EtOH to produce 2,3,7,8-tetrakis(methylthio)-1,4,6,9-tetraethyl thianthrene (**11**) and bis[2,3,5-tris(methylthio)-1,4-diethyl phenyl]sulfide (**12**). Compound **11**: mp 118–119°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 1.29 (t, $J=7.4$ Hz, 12H), 2.42 (s, 12H), 3.41 (q, $J=7.4$ Hz, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 15.6, 21.9, 28.6, 137.8, 142.0, 146.8; MS (m/z) 512 (M^+); anal. calcd for $\text{C}_{24}\text{H}_{32}\text{S}_6$: C, 56.20; H, 6.29. Found: C, 56.41; H, 6.57; compound **12**: mp 108–109°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 0.86 (t, $J=7.3$ Hz, 6H), 1.17 (t, $J=7.3$ Hz, 6H), 2.19 (s, 3H), 2.40 (s, 3H), 2.43 (s, 3H), 3.25 (q, $J=7.3$ Hz, 4H), 3.35 (q, $J=7.3$ Hz, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 15.2, 16.3, 21.2, 21.8, 22.1, 29.3, 29.7, 140.8, 142.6, 144.4, 145.4, 150.6, 152.7; MS (m/z) 574 (M^+); anal. calcd for $\text{C}_{26}\text{H}_{38}\text{S}_7$: C, 54.30; H, 6.66. Found: C, 54.63; H, 6.67.
16. The initial intermediate of the photolytic dimerization reaction of **5** has not been identified.