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Preparation of Functionalized Thianthrenes and Their Higher Related Compounds by Photolysis of Benzotrithiole Derivatives

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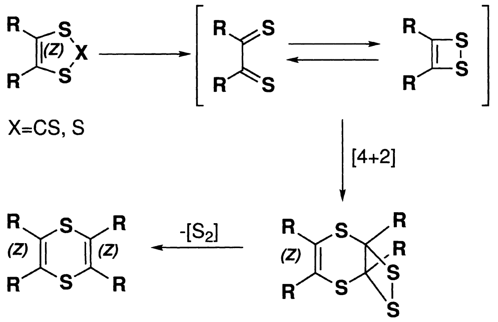
6,9-Diethyl-1,2,3,4,5-benzopentathiepin (**1**) and 4,7-diethyl-1,2,3-benzotrithiole (**2**) were photolyzed by a 100 W high-pressure mercury lamp in dichloromethane under an argon atmosphere. These reactions produced 1,4,6,9-tetraethylthianthrene (**3**) by way of desulfurization, dimerization, and ring contraction reactions. Application of the photolysis was possible to 4,8-diethylbenzo[1,2-*d*:4,5-*d′*]di[1,2,3]trithiole (**6**) and 4,7-diethyl-5,6-ethylenedithio-1,2,3-benzotrithiole (**7**). These reactions provided 1,4,6,9-tetraethyl[4,5-*b*:4′,5′-*i*]di[1,2,3]trithiolothianthrene (**8**) with two trithiole rings and 1,4,6,9-tetraethyl-2,3:7,8-bis(ethylenedithio)thianthrene (**10**) with two ethylenedithio groups on both sides of thianthrene, respectively. The photolysis of 1,4,6,9-tetraethyl-7,8-bis(octylthio)[1,2,3]trithiolo[4,5-*b*]thianthrene (**12**) and 1,4,6,9-tetraethyl-7,8-ethylenedithio[1,2,3]trithiolo[4,5-*b*]thianthrene (**15**) gave higher related derivatives of thianthrene, 1,4,6,8,10,13,15,17-octaethyl-2,3,11,12-tetrakis(octylthio)-5,7,9,14,16,18-hexathiaheptacene (**14**) and 1,4,6,8,10,13,15,17-octaethyl-2,3:11,12-bis(ethylenedithio)-5,7,9,14,16,18-hexathiaheptacene (**16**), respectively. The electrochemical property of each thianthrene derivative was verified by cyclic voltammetry using silver nitrate as a reference electrode.

Thianthrene and related compounds have been the focus of attention regarding their radical cations, charge-transfer complexes, and metal complexes.[1] There have been many reports about the synthesis, structure, reactions, and electrochemical properties of thianthrene, selenanthrene and telluranthrene derivatives. Several 1,4-dithiins were obtained by the photolysis of 1,3-dithiole-2-thion and 1,2,3-trithiole derivatives (Eq. 1).[2]



(1)

Such reactions proceeded by way of generation of 1,2-dithion, its isomerization to 1,2-dithiete,[3–6] [4 + 2] cycloaddition of 1,2-dithion with 1,2-dithiete, and elimination of diatomic sulfur "S_2".[7] During our studies into the several cyclic polysulfides,[8,9] when 6,9-diethyl-1,2,3,4,5-benzopentathiepin (**1**) was photolyzed in dichloromethane, 4,7-diethyl-1,2,3-benzotrithiole (**2**) and 1,4,6,9-tetraethylthianthrene (**3**) were obtained by a degradation reaction of the pentathiepin ring and a subsequent dimerization reaction. The photolysis of **2** also gave **3** in a moderate yield. These results led us to expect that these photolytic reactions would provide a method for preparation of new thianthrene derivatives with several sulfur functional groups. For instance, the photolysis of 4,8-diethylbenzo[1,2-*d*:4,5-*d′*]di[1,2,3]trithiole (**6**) gave the dimerized molecule, 1,4,6,9-tetraethyl[4,5-*b*:4′,5′-*i*]di[1,2,3]trithiolothianthrene (**8**), which bears two trithiole rings on both sides of thianthrene; hexathiaheptacenes, as higher related compound of thianthrene, were obtained by the similar photolytic dimerization reaction. This article reports novel photolytic reactions of benzotrithioles and related compounds producing several functionalized thianthrene derivatives and their higher derivatives.

Results and Discussion

In our previous studies, benzopentathiepin and benzotrithiole were found to be kinetically stabilized by two substituents at the ortho positions; benzopentathiepin with no substituent decomposed gradually in light to produce an insoluble material, while unsubstituted benzotrithiole could not be isolated as a stable form. To examine the photolytic reaction of benzopentathiepin and benzotrithiole, their typical compounds, **1** and **2** with two ethyl groups were irradiated with a 100 W high-pressure mercury lamp in dichloromethane under an argon atmosphere, because of the stability and solubility of the products.

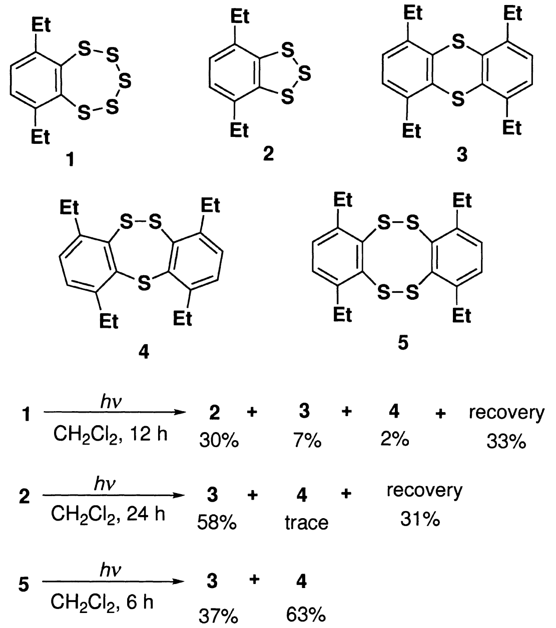
The photolytic reaction of **1** gave **2**, **3**, and 1,4,7,10-tetraethyldibenzo[*c*,*f*][1,2,5]trithiepin (**4**) in 30%, 7%, and 2% yields, respectively (Scheme 1), while the photolysis of **2** produced **3** in 58% yield together with a trace amount of **4**.

In the photoreaction of **1** and **2**, elemental sulfur was detected as a byproduct in the separation process by column chromatography. The initial intermediates, derived from **1** and **2**, were not identified in the photolytic reaction; however, it appeared that the irradiation of **1** induced the elimination of two sulfur atoms from the pentathiepin ring to give **2**; compound **2** was degraded via the consecutive ring-opening, desulfurization and intermolecular recombination reactions to produce a dimerized molecule. So we wanted to determine whether or not 1,4,7,10-tetraethyldibenzo[*c*,*g*][1,2,5,6]tetrathiocin (**5**) is one of the intermediates in the photoreaction of **1** and **2**.[10] Compound **5** was prepared by treatment of 4,7-diethyl-2,2-dimethyl-1,3,2-benzodithiastannole with *n*-butyl lithium in tetrahydrofuran, and then with oxygen for the oxidative dimerization (60%);[8b] compound **5** had good solubility in the usual organic solvents at room temperature. When **5** was photolyzed in dichloromethane under an argon atmosphere for 6 h, **3** and **4** were obtained in 37% and 63% yields, respectively (Scheme 1). Irradiation of **5** in dichloromethane for 48 h gave **3** in 98% yield. These results suggest that the photolysis of **5** initially provided **4** by extrusion of one sulfur atom from the tetrathiocin ring, and **4** was further desulfurized to produce **3**. Although it was reported that several 1,4-dithiins were obtained by [4 + 2] cycloaddition of 1,2-dithion with 1,2-dithiete, and succeeding elimination of diatomic sulfur "S_2", as shown in Eq. 1, the ring contraction reaction of **5** should proceed by a stepwise elimination of one sulfur atom by way of **4** as an intermediate. Meanwhile, since 1,2-dithietes gave corresponding tetrathiocin derivatives by dimerization reaction,[5,6] **5** was expected to be a dimerized intermediate in the photolysis of **1** and **2**.

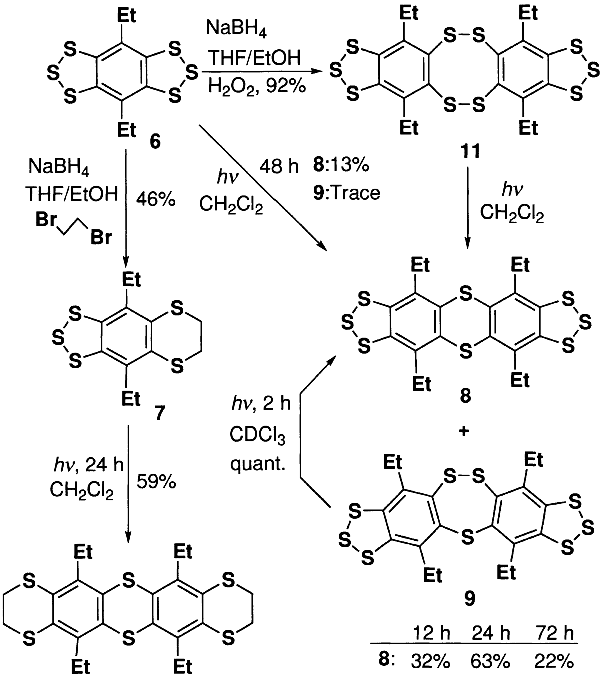
For preparation of a thianthrene derivative with two trithiole rings as a functional group, we applied the photolytic dimerization reaction of benzotrithiole **2** to **6**, since no desulfurization reagent was essential in the photoreaction. By the photolysis of **6** for 48 h, **8** was obtained in 13% yield together with a trace amount of 1,4,7,10-tetraethyl[4,5-*b*:4′,5′-*j*]di[1,2,3]trithiolodibenzo[*c*,*f*][1,2,5]trithiepin (**9**) (Scheme 2). Compound **6** was photolyzed under several photolytic reaction conditions; on prolonging the reaction time, however, the yield of **8** was decreased gradually, accompanied with production of unidentified insoluble material.

The yield of **8** was decreased on prolonging the reaction time; hence, it is important to examine the photolytic reactivity of **6** and **8**. In the UV spectra measured in dichloromethane, the absorption wavelength of **8** is similar to that of **6** (Table 1), suggesting that photolytic reactivity of **8** was similar to that of **6**; compound **8**, obtained by the photolysis, was further desulfurized under the reaction conditions to produce an insoluble material. To demonstrate the further photoreaction of the trithiole rings of the product, 4,7-diethyl-5,6-ethylenedithio-1,2,3-benzotrithiole (**7**) was prepared on treatment of **6** with sodium borohydride and then 1,2-dibromoethane (Scheme 2). When **7** was photolyzed in dichloromethane for 24 h, 1,4,6,9-tetraethyl-2,3:7,8-bis(ethylenedithio)thianthrene (**10**) was produced in 59% yield as colorless crystals. Compound **10** was more stable than **8** under the reaction conditions, revealing that **8** decomposed due to further photoreaction of the trithiole ring.

To us, the ring contraction reaction of dibenzotetrathiocin **5** is more advantageous than the dimerization reaction of benzotrithiole **2** for preparation of thianthrene (Scheme 1). To prepare **8** in an acceptable yield, we first prepared 1,4,7,10-tetra-



Scheme 1.



Scheme 2.

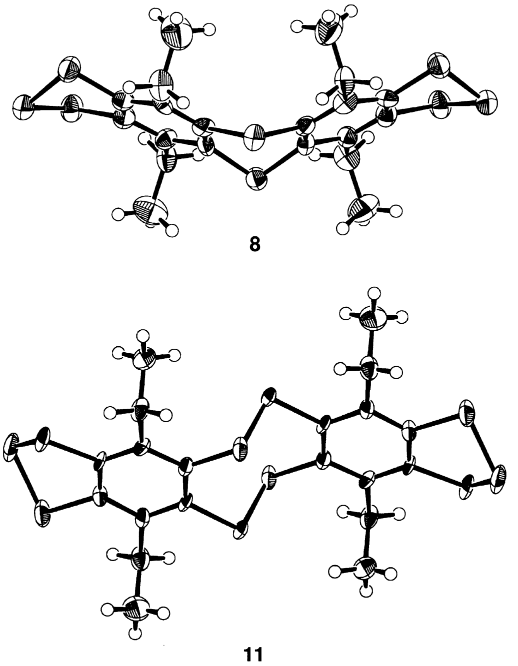
Table 1. UV Spectra[a)]

	UV			
	λ_{max}/nm(ε)			
1	299	(3600)	355	(1200)[b)]
2	274	(7100)	325	(1500)
3	287	(4700)	295	(4300)
5	317	(7500)	350	(2500)[b)]
6	297	(17000)	353	(2500)
7	288	(18000)	341	(2800)[b)]
8	294	(37000)	341	(6200)
9	296	(21900)	342	(5600)
10	313	(11000)[b)]	326	(7500)[b)]
11	300	(36000)	361	(12000)
12	289	(68000)	361	(14000)[b)]
14	287	(72000)	324	(22000)
15	326	(5500)[b)]	337	(4200)[b)]

a) The UV spectra were measured in CH_2Cl_2. b) shoulder.

ethyl[4,5-*b*:4′,5′-*i*]di[1,2,3]trithiolodibenzo[c,*g*][1,2,5,6]tetrathiocin (**11**) in 92% yield on treatment of **6** with sodium borohydride in tetrahydrofuran and ethanol, and then with hydrogen peroxide for the oxidative dimerization (Scheme 2).

The structures of **8** and **11** were determined by X-ray crystallographic analysis (Fig. 1). The ORTEP drawing reveals that **8** has two trithiole rings on each side of thianthrene. The bond lengths and bond angles of the trithiole and central dithiin rings of **8** are similar to those of the benzotrithioles and thianthrenes reported in the literature.[8,9,11] Meanwhile, it was reported that the tetrathiocin derivatives exist as two conformations: a chair conformation and a twist conformation.[12] The ORTEP drawing reveals that **11** has one tetrathiocin and two trithiole rings, and the tetrathiocin ring is in a chair conformation in the crystal structure. The bond length and bond angles of the trithiole and tetrathiocin rings are similar to those reported for benzotrithiole and dibenzotetrathiocin derivatives.



8

11

Fig. 1. The ORTEP drawings of **8** and **11**.

The absorption wavelengths (λ_{max}) of **6**, **8** and **11** exist in a similar region in the UV spectra, while the molar absorptivity (ε) of **11** is higher than those of **6** and **8** (Table 1). Thus, the photoreaction of **11** was expected to be favorable compared with that of **6** and **8**; however, **11** had low solubility in usual organic solvents at room temperature, in contrast to the solubilities of **6** and **8**. For this reason, irradiation was performed in the suspension of **11** in dichloromethane under several reaction conditions. When **11** was photolyzed for 12 h, **8** and **9** were obtained in 32% and 34% yields, respectively. The similar irradiation of **11** for 24 h gave **8** in 63% yield together with **9** in 10% yield. When the reaction time was prolonged to 72 h, the yield of **8** and **9** decreased to 22% and 8% yields, respectively. These results reveal that the photolysis of **11** proceeded faster than those of **6** and **8** under the reaction conditions, and **9** was initially generated by elimination of one sulfur atom from **11**, and further desulfurized to give **8**.

Our previous paper reported that a 1:1 mixture of **8** and **9** that had been prepared by the photolysis of **11** was photolyzed in $CDCl_3$, revealing that **9** is an intermediate in the photolysis of **11**.[9c] It was difficult to purify the compound **9**, because **9** has similar solubility and crystallinity to **8**, and it decomposed slowly to produce **8** and elemental sulfur. For examination of the photolysis of pure **9**, compound **9** was repeatedly recrystallized from dichloromethane/methanol under the dark condition; that process gave **9** as pure orange crystals. Irradiation of **9** was performed for 2 h to produce **8** in a quantitative yield (Scheme 2), and the reaction seemed to proceed faster than that of **6** and **8**. The absorption wavelength (λ_{max}) of **9** is similar to those of **6** and **8** (Table 1), while the elongation of the absorption region of **9** to about 450 nm, different from those of **6** and **8**, may be beneficial for the photolysis of **9**. Since the reaction was expected to be a unimolecular elimination reaction of one sulfur atom from the central trithiepin ring, purified **9** was dissolved in deuterated chloroform, and the photolysis was monitored by ^1H NMR spectroscopy to determine the kinetic parameter of the reaction (Fig. 2). In the spectra, de-

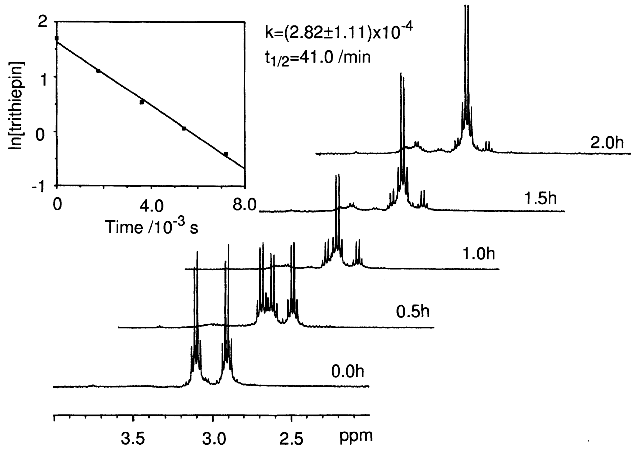
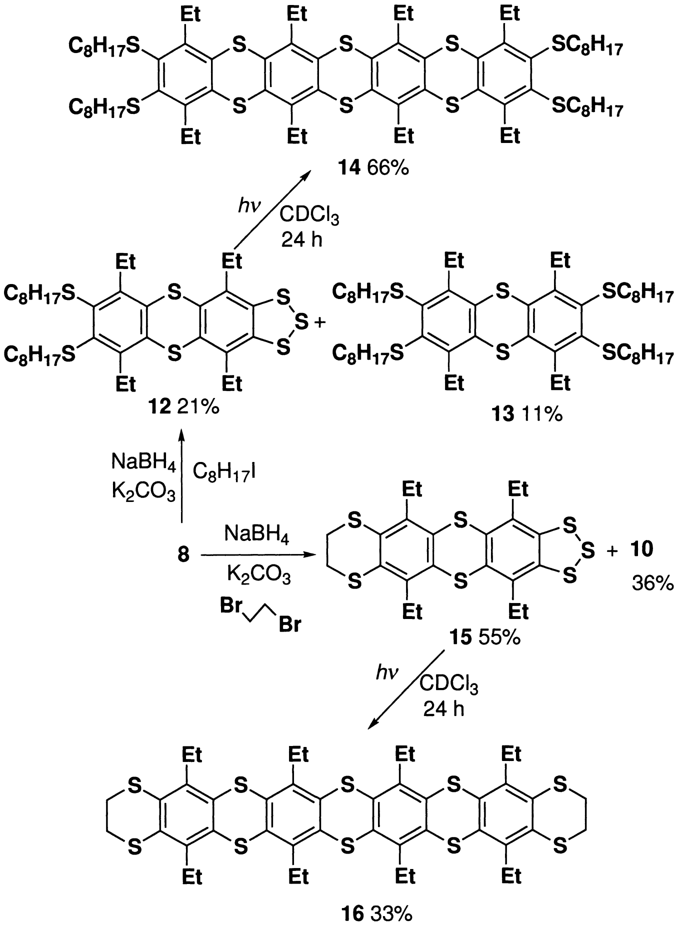


Fig. 2. ^1H NMR stack plot of photolysis of **9**. Inset: firstorder plot, [trithiepin]:concentration of **9**.

crease of the signal of **9** and appearance and increase of the new signal of **8** were observed. By the result of the plot of ln[trithiepin] versus the reaction time, the desulfurization reaction of **9** was determined as to be first order with respect to the decrease of the substrate; [trithiepin] is the concentration of **9** (Fig. 2 Inset). The parameters are calculated as k = (2.82 ± 1.11) × 10^{-4} for the rate constant, and as $t_{1/2}$ = 41.0 min for the half-life of the photoreaction. These results imply that the photolysis of **11** proceeded by the stepwise sulfur extrusion reaction via **9** as an intermediate.

It was interested in construction of a higher related derivative of thianthrene such as a polythia ladder molecule.[1,13] In these molecules, the double-stranded structures are expected to possess unique electronic properties compared with those of a single-stranded molecule such as polyphenylene sulfide. To prepare that molecule, the photolytic dimerization reaction was examined by using several benzotrithiole derivatives. Initially, **8** was photolyzed by the method as described above, under the diluted conditions; however, we could not control the photolysis of **8**, and an insoluble material was obtained together with a recovery of the starting compound. As a result of this reaction, **8** was treated with sodium borohydride, potassium carbonate, and then octyl iodide, to produce 1,4,6,9-tetraethyl-7,8-bis(octylthio)[1,2,3]trithiolo[4,5-*b*]thianthrene (**12**) in 21% yield together with 1,4,6,9-tetraethyl-2,3,7,8-tetrakis(octylthio)thianthrene (**13**) in 11% yield (Scheme 3). Compound **12** is more soluble in organic solvents than other thianthrene derivatives. Then **12** was dissolved in deuterated chloroform in an NMR tube, and photolyzed under an argon atmosphere. The reaction was monitored by ^{1}H NMR spectroscopy. After irradiation for 24 h and purification by a preparative HPLC, a ladder-type thianthrene, 1,4,6,8,10,13,15,17-octaethyl-2,3,11,12-tetrakis(octylthio)-5,7,9,14,16,18-hexathiaheptacene (**14**) was obtained in 66% yield as colorless powder. The structure of **14** was determined by ^{1}H NMR spectroscopy and elemental analysis. The molecular weight of **14** was also determined by MALDI-TOF MS as m/z = 1292.41 (M^+). Compound **14** was soluble in several organic solvents such as dichloromethane, chloroform and tetrahydrofuran; however, we could not obtain **14** as crystals suitably for X-ray crystallography.

Since the preparation of **14** was carried out by a dimerization reaction of **12**, we tried to prepare a related compound with two ethylenedithio groups. Compound **8** was reacted with sodium borohydride and 1,2-dibromoethane, which produced 1,4,6,9-tetraethyl-7,8-ethylenedithio[1,2,3]trithiolo[4,5-*b*]thianthrene (**15**) with one trithiole ring and one ethylenedithio group on each side of thianthrene in 55% yield, together with **10** in 36% yield. Then photolysis of **15** was performed as described above. After irradiation for 24 h, a colorless precipitate was separated by filtration. The precipitate was identified



Scheme 3.

Table 2. Oxidation Potentials

	$E_{1/2}$/V	
2[a]	0.71	
3[a]	0.89	
6[c]	0.83	0.95
7[b]	0.78	1.12
8[c]	0.88[d]	
10[b]	0.80	1.02
12[b]	0.92	1.25[d]
13[b]		1.04
14[b]		1.10[d]
15[b]	0.87	1.00

a) Measured in CH_3CN. b) Measured in CH_2Cl_2. c) Measured in CH_2Cl_2:CH_3CN = 1:1. d) Quasi reversible (E_p/V).

as a dimerized product 1,4,6,8,10,13,15,17-octaethyl-2,3:11,12-bis(ethylenedithio)-5,7,9,14,16,18-hexathiaheptacene (**16**) by the measurements of ^{1}H NMR and MALDI-TOF MS. Compound **16** was obtained in 33% yield; however, **16** was difficult to purify because of its low solubility in usual organic solvents.

Benzotrithiole and thianthrene were reported to show reversible redox potential by cyclic voltammetry measurements, and to produce stable radical cations by single electron oxidation.[8,10] Compound **8** consists of benzotrithiole and thianthrene, and is expected to have electrochemical property related to that of **2** and **3**. To examine the electrochemical properties of thianthrene and benzotrithiole derivatives, their oxidation potentials were measured by cyclic voltammetry by using silver nitrate as a reference electrode (Table 2). Compound **2** showed one reversible redox potential at $E_{1/2}$ = 0.71 V and **3** showed one at $E_{1/2}$ = 0.89 V. Alternatively, as shown in Fig. 3, two reversible redox potentials were recorded for **6** ($E_{1/2}$ = 0.83, 0.95 V), **7** ($E_{1/2}$ = 0.78, 1.12 V), **10** ($E_{1/2}$ = 0.80, 1.02 V; not indicated), and **15** ($E_{1/2}$ = 0.88, 1.01 V). Among these four compounds, **7** has the largest potential difference between the first and second oxidation potentials. Meanwhile, **15** has a higher first oxidation potential than **7** and a lower second oxidation potential as well, suggesting that the potential differences between the first and second oxidation potentials of **7** and **15** are affected by the abilities of the central benzene ring and thianthrene to stabilize the radical cation and bis(radical cation), and to relax the Coulomb repulsion between two radical cations generated by first and second oxidations. Due to similar effects of the central benzene ring and thianthrene, the first and second oxidation potentials of **8** are expected to be in closer proximity than those of **6**; thus the cyclic voltammogram of **8** is observed as one quasi-reversible peak (E_p = 0.88 V). Compound **13** showed one reversible redox potential at $E_{1/2}$ = 1.04 V. However, the cyclic voltammogram of **14** was recorded as one quasi-reversible peak (E_p = 1.10 V), which is predicted to arise from a multi-center electron transfer of this molecule.

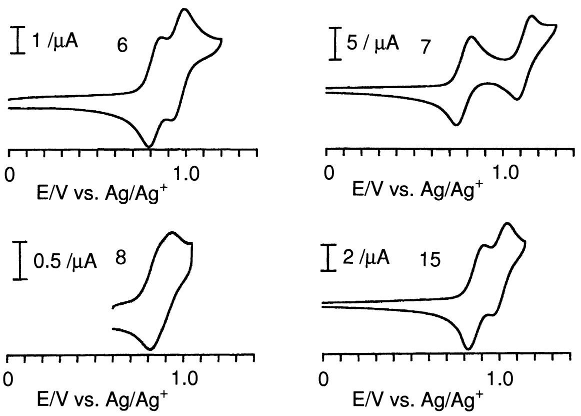


Fig. 3. Cyclic voltammograms of **6**, **7**, **8**, and **15**.

Conclusion

Photolytic desulfirization, dimerization, and ring-contraction reactions of several benzotrithioles were performed by irradiation with a 100 W high-pressure mercury lamp to produce the corresponding thianthrenes. It was expected that the photolysis of benzopentathiepin and benzotrithiole proceeded by way of dibenzotetrathiocin and dibenzotrithiepin derivatives as intermediates; dibenzotetrathiocin provided dibenzotrithiepin by extrusion of one sulfur atom from the tetrathiocin ring, and dibenzotrithiepin was further desulfirized to produce thianthrene. These reactions gave thianthrene derivatives with the trithiole ring and the ethylenedithio group, and their higher related derivatives, hexathiaheptacenes.

Experimental

General. NMR spectra were measured with a Bruker AC-400 spectrometer. IR spectra were recorded on a JASCO FT-7300 spectrometer. MS were obtained with a Hitachi M-2000 mass spectrometer. MALDI-TOF MS (matrix assisted laser desorption ionization-time of flight mass spectrometry) were examined with a PerSeptive Biosystems Voyager RP-DE mass spectrometer. UV spectra were measured with a JASCO Ubest-30 spectrometer. For measurement of oxidation potential, a Toa Electronics Ltd. Model CS-1090 apparatus was used. Elemental analyses were performed on a Yanako MT5 analyzer. For X-ray crystallographic analysis, the data collection was made on a Rigaku AFC7R diffractometer employing Cu $K\alpha$ radiation and a 12 kW rotating anode generator. All calculations were performed using teXsan Structure Analysis Package, Molecular Structure Corp. (1985 and 1992).

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 144420 and 191961. The complete data are deposited as Document No. 75049 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Oxidation Potentials. All measurements were performed by cyclic voltammetry, using Ag/0.01 M (1 M = 1 moldm^{-3}) $AgNO_3$ as a reference electrode. The electrolyte was 0.1 M NH_4ClO_4; CH_3CN, CH_2Cl_2, and CH_3CN:CH_2Cl_2 = 1:1 were used as solvents. The scan rate was 200 mVs^{-1} for all measurements.

6,9-Diethyl-1,2,3,4,5-benzopentathiepin (1) and 4,7-Diethyl-1,2,3-benzotrithiole (2). Compounds **1** and **2** were prepared from 4,7-diethyl-2,2-dimethyl-1,3,2-benzodithiastannole in 60% and 30% yields by a similar method to that previously reported.[8b,14]

Photolysis of 1. Compound **1** (44 mg, 0.15 mmol) was placed in a glass tube, and CH_2Cl_2 (23 mL) was added under Ar. The solution was irradiated with a 100 W high pressure mercury lamp for 12 h. After distillation of the solvent, the products were purified by column chromatography (silica gel, hexane) to produce **2**, **3**, and **4** in 30%, 7% and 2% yields. The yields of **3** and **4** were determined by ^{1}H NMR of a mixture of these compounds, since the compound **4** could not be isolated. Compound **3** was obtained as pure crystals by repeated recrystallization; **3**: mp 101.5–102.0 °C (decomp); ^{1}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}C NMR (101 MHz, $CDCl_3$) δ 15.3, 27.9, 127.3, 136.0, 141.5; MS *m*/*z* 328 (M^+); Anal. Found: C, 72.89; H, 7.54%. Calcd for $C_{20}H_{24}S_2$: C, 73.12; H, 7.36%; **4**: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J = 7.5 Hz, 6H), 1.27 (t, J = 7.5 Hz, 6H), 2.79 (q, J = 7.5 Hz, 4H), 3.01 (q, J = 7.5 Hz, 4H), 7.04, 7.12 (ABq, J = 7.6 Hz, 4H); MS *m*/*z* 360 (M^+).[15]

Photolysis of 2. Compound **2** (102 mg, 0.45 mmol in 68 mL of CH_2Cl_2) was photolyzed for 24 h under Ar. After distillation of the solvent and purification by column chromatography (silica gel, hexane), **3** was obtained in 58% yield (51 mg) together with a trace amount of **4**.

1,4,7,10-Tetraethyldibenzo[*c*,*g*][1,2,5,6]tetrathiocin (5). To a solution of 4,7-diethyl-2,2-dimethyl-1,3,2-benzodithiastannole (446 mg, 1.3 mmol) in THF (25 mL), *n*-BuLi (1.66 M, 1.57 mL, 2.6 mmol) was added slowly at 0 °C under N_2, and the solution was stirred for 10 min at room temperature. The benzenedithiolate anion generated in the solution was oxidized by oxygen for 1.5 h. Then the solution was treated with an aqueous HCl solution and extracted with CH_2Cl_2. After distillation of the solvent and purification by column chromatography (silica gel, CCl_4), **5** was obtained in 60% yield (150 mg); **5**: mp 209.0–210.0 °C; ^{1}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}C NMR (101 MHz, $CDCl_3$) δ 16.4, 29.7, 131.1, 142.1, 148.3; MS *m*/*z* 392 (M^+); Anal. Found: C, 61.23; H, 5.96%. Calcd for $C_{20}H_{24}S_4$: C, 61.18; H, 6.16%.

Photolysis of 5. Method A: Compound **5** (105 mg, 0.26 mmol) was placed in a glass tube, and CH_2Cl_2 (39 mL) was added under Ar. The solution was irradiated for 6 h. After distillation of the solvent, the product was purified by column chromatography (silica gel, hexane) to give **3** and **4** in 37% and 63% yields, respectively. The yields were determined by ^{1}H NMR spectrum.

Method B: Compound **5** (22 mg, 0.06 mmol) was photolyzed in CH_2Cl_2 (20 mL) under Ar for 48 h. After purification by column chromatography (silica gel, CCl_4 : hexane = 1 : 1), **3** was obtained in 98% yield (18 mg).

1,4,6,9-Tetraethyl[4,5-*b*:4′,5′-*i*]di[1,2,3]trithiolothianthrene (8) and 1,4,7,10-Tetraethyl[4,5-*b*:4′,5′-*j*]di[1,2,3]trithiolodibenzo[*c*,*f*][1,2,5]trithiepin (9). Compound **6** (37 mg, 0.11 mmol) was placed in a glass tube, and CH_2Cl_2 (15 mL) was added under Ar. The solution was irradiated with a 100 W high pressure mercury lamp for 48 h. After distillation of the solvent, the residue was purified by column chromatography (silica gel, hexane), **8** was obtained in 13% yield (4 mg) together with a trace amount of **9**; **8**: mp 237–238 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, J = 7.5 Hz, 12H), 3.03 (q, J = 7.5 Hz, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.2, 30.5, 136.2, 137.2, 141.3; MS *m*/*z* 516 (M^+); Anal. Found: C, 46.49; H, 3.99%. Calcd for $C_{20}H_{20}S_8$: C, 46.47; H, 3.90%. The crystal data for **8**: tetragonal, $P\bar{4}$ (#81), a = 23.545(1) Å, c = 4.824(2) Å, V = 2674.2(7) Å^3, Z=4, D_c = 1.28 g/cm^3, μ (Cu $K\alpha$) = 62.1 cm^{-1}, R = 0.062 (Rw = 0.099), GOF = 1.14; **9**: mp 135 °C; ^{1}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); ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.9, 14.1, 30.0, 31.2, 133.2, 137.8, 139.5, 140.9, 141.4, 142.5; MS *m*/*z* 548 (M^+); Anal. Found: C, 43.49; H, 3.55%. Calcd for $C_{20}H_{20}S_9$: C, 43.76; H, 3.67%.

4,7-Diethyl-5,6-ethylenedithio-1,2,3-benzotrithiole (7). To a solution of **5** (179 mg, 0.55 mmol) in THF (20 mL) and ethanol (20 mL), $NaBH_4$ (23 mg, 0.6 mmol) was added slowly, and the solution was stirred at room tenperature for 15 min. After treatment with H_2O (5 mL), 1,2-dibromoethane (0.95 mL, 11 mmol) was added, and the solution was stirred for 12 h. After usual work-up, the solution was extracted with CH_2Cl_2 and the solvent was evaporated. The residue was purified by column chromatography (silica gel, CCl_4 : hexane = 1 : 1) to produce **7** in 46% yield (82 mg); **7**: mp 114–116 °C; ^{1}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, CH_2); MS *m*/*z* 318 (M^+); Anal. Found: C, 45.29; H, 4.38%. Calcd for $C_{12}H_{14}S_5$: C, 45.24; H, 4.43%.

1,4,6,9-Tetraethyl-2,3:7,8-bis(ethylenedithio)thianthrene (10). Compound **7** (32 mg, 0.10 mmol) in CH_2Cl_2 (15 mL) was irradiated as described above for 24 h. After distillation of the solvent and purification by column chromatography (silica gel, CCl_4), **10** was obtained in 59% yield (17 mg) together with the recovery of **7** in 22% yield (7 mg); **10**: mp 239–242 °C; ^{1}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}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. Found: C, 56.35; H, 5.34%. Calcd for $C_{24}H_{28}S_6$: C, 56.65; H, 5.55%.

1,4,7,10-Tetraethyl[4,5-*b*:4′,5′-*j*]di[1,2,3]trithiolodibenzo[*c*,*g*][1,2,5,6]tetrathiocin (11). To a solution of **6** (323 mg, 1.0 mmol) in THF (20 mL) and ethanol (5 mL), $NaBH_4$ (38 mg, 1.0 mmol) was added slowly, and the solution was stirred for 30 min. After addition of aqueous HCl solution (4 mL), H_2O_2 (0.1 mL, 1.0 mmol) was added, and the solution was stirred for 30 h. The yellow precipitate was filtered under reduced pressure, and **11** was obtained in 92 % yield (267 mg). The compound **11** was purified by recrystallization from CH_2Cl_2; **11**: mp 239.5–241.5 °C; ^{1}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 ($M^+ - 64$); Anal. Found: C, 41.15; H, 3.60%. Calcd for $C_{20}H_{20}S_{10}$: C, 41.34; H, 3.47%; the crystal data for **11**: monoclinic: $P2_1/a$, a = 9.404(3) Å, b = 9.859(2) Å, c = 13.528(2) Å, β = 105.69(1)°, V = 1207.5(4) Å^3, Z = 2, D_c = 1.598 g/cm^3, μ (Cu $K\alpha$) = 85.26 cm^{-1}, R = 0.048 (Rw = 0.072).

Photolysis of 11. Compound **11** (291 mg, 0.50 mmol) in CH_2Cl_2 (200 mL) was irradiated for 24 h under Ar. After distillation of the solvent, the product was purified by column chromatography (silica gel, hexane) to give **8** in 63% yield together with **9** in 10% yield. The yields of **8** and **9** were determined by the integral ratio of ^{1}H NMR.

1,4,6,9-Tetraethyl-7,8-bis(octylthio)[1,2,3]trithiolo[4,5-*b*]thianthrene (12) and 1,4,6,9-Tetraethyl-2,3,7,8-tetrakis(octylthio)thianthrene (13). To a solution of **8** (104 mg, 0.2 mmol) in THF (60 mL) and ethanol (10 mL), $NaBH_4$ (8 mg, 0.2 mmol) was added slowly and the solution was stirred for 30 min. After addition of K_2CO_3 (83 mg, 0.6 mmol), the solution was stirred for 30 min. Then octyl iodide (0.55 mL, 3.0 mmol) was added, and the solution was refluxed for 24 h. After usual workup, the solution was extracted with CH_2Cl_2 and the solvent was evaporated. The residue was purified by column chromatography (silica gel, hexane) and preparative HPLC to produce **12** and **13** in 22% (32 mg) and 11% (20 mg) yields, respectively; **12**: yellow crystal; mp 42.0–43.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 6.9 Hz, 6H), 1.22–1.30 (m, 28 H), 1.33–1.39 (m, 4H), 1.52–1.59 (m, 4H), 2.87 (t, J = 7.4 Hz, 4H), 3.07 (q, J = 7.5 Hz, 4H), 3.38 (q, J = 7.5 Hz, 4H); Anal. Found: C, 60.86; H, 7.65%. Calcd for $C_{36}H_{54}S_7$: C, 60.79; H, 7.65%; **13**: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 6.9, 12H), 1.24–1.30 (m, 44H), 1.36–1.39(m, 8H), 1.54–1.59 (m, 8H), 2.87 (t, J = 7.4 Hz, 8H), 3.41 (q, J = 7.5 Hz, 8H); Anal. Found: C, 69.09; H, 10.08%. Calcd for $C_{52}H_{88}S_6$: C, 68.96; H, 9.79%.

1,4,6,8,10,13,15,17-Octaethyl-2,3,11,12-tetrakis(octylthio)-5,7,9,14,16,18-hexathiaheptacene (14). Compound **12** (30 mg, 0.04 mmol) was placed in an NMR tube, and $CDCl_3$ (0.55 mL) was added under argon. The solution was irradiated with a 100 W high-pressure mercury lamp for 24 h. After distillation of the solvent, the reaction mixture was purified by column chromatography (silica gel, hexane) and preparative HPLC. By such a process, **14** was obtained in 66% yield (17 mg); **14**: colorless powder; mp 179–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, J = 6.9 Hz, 12H), 1.21–1.30 (m, 56 H), 1.30–1.38 (m, 8H), 1.49–1.58 (m, 8H), 2.84 (t, J = 7.4 Hz, 8H), 3.38 (q, J = 7.0 Hz, 8H), 3.40 (q, J = 7.0 Hz, 8H); MALDI-TOF MS *m/z* 1292.41 (M^+); Anal. Found: C, 66.97; H, 8.47%. Calcd for $C_{72}H_{108}S_{10}$: C, 66.81; H, 8.41%.

1,4,6,9-Tetraethyl-7,8-ethylenedithio[1,2,3]trithiolo[4,5-*b*]thianthrene (15). To a solution of **8** (155 mg, 0.3 mmol) in THF (100 mL) and ethanol (10 mL), $NaBH_4$ (11 mg, 0.3 mmol) was added slowly, and the solution was stirred for 30 min. After addition of K_2CO_3 (124 mg, 0.9 mmol), the solution was stirred for 30 min. Then 1,2-dibromoethane (0.5 mL, 6.0 mmol) was added and the solution was refluxed for 24 h. After usual workup, the solution was extracted with CH_2Cl_2 and the solvent was evaporated. The residue was purified by column chromatography (silica gel, $CHCl_3$: hexane = 1 : 5) to produce **15** in 55% yield (85 mg) together with **10** in 36% yield (55 mg); **15**: mp 174–176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, J = 7.4 Hz, 6H), 1.24 (t, J = 7.4 Hz, 6H), 3.06 (q, J = 7.4 Hz, 4H), 3.18 (s, 4H), 3.20 (q, J = 7.4 Hz, 4H); MS *m/z* 512 (M^+); Anal. Found: C, 51.88; H, 4.74%. Calcd for $C_{22}H_{24}S_7$: C, 51.51; H, 4.72%.

1,4,6,8,10,13,15,17-Octaethyl-2,3 : 11,12-bis(ethylenedithio)-5,7,9,14,16,18-hexathiaheptacene (16). Compound **15** (20 mg, 0.04 mmol) was placed in an NMR tube, and $CDCl_3$ (0.55 mL) was added under argon. The solution was irradiated with a 100 W high-pressure mercury lamp. After 24 h, the reaction mixture was filtered and washed with dichloromethane (33% yield; 6 mg); **16**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, J = 7.5 Hz, 12H), 1.30 (t, J = 7.5 Hz, 12H), 3.15 (s, 8H), 3.19 (q, J = 7.5 Hz, 8H), 3.37 (q, J = 7.5 Hz, 8H); MALDI-TOF MS *m/z* 896.04 (M^+).

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