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Synthesis and Structure of Sulfur-Bridged [1.$_n$](2,5)Thiophenophanes (n = 4—6)

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Sulfur-bridged [1.$_n$](2,5)thiophenophanes (n = 4—6) were prepared by cyclization of dibromo derivatives of the corresponding linear oligo(thio-2,5-thienylenes) (**1**) on reactions with Na_2S. The best results were obtained by heating **1** and Na_2S in the presence of Cs_2CO_3 in NMP (24% yield for n = 4, 16% for n = 5, and 10% for n = 6). The reactions gave less satisfactory results either in the presence of CuI (Cu_2O) or in the absence of these additives. The results of the X-ray structural analyses of these three compounds are also reported.

Poly(thio-1,4-phenylene) [poly(p-phenylene sulfide)] (**1**) is a high-performance polymer whose synthesis and industrial use have been extensively studied. Meanwhile, the chemistry of poly(thio-2,5-thienylene) (**2**) has been much less investigated than that of **1**.[1)] Keeping this in mind, we have investigated the preparation of a series of oligo(thio-2,5-thienylenes) (**3**) (n = 1—4) and their dibromo derivatives (Chart 1).[2)] As a natural consequence of this study, our next target was focused on the conversion of **3** into the corresponding cyclic oligomers, [1.$_n$] (2,5)thiophenophanes (**4**). These cyclic compounds are a thiophene counterpart of oligo(p-phenylene sulfides) (**5**) whose syntheses have been studied in detail.[3)] The thiophenophanes **4** would be important as thiacrown ethers and also sulfur-bridged calixarene-like molecules which function as host molecules to soft and heavy metal ions. In relation with this problem, syntheses and properties of cyclic compounds, such as **6**,[4)] **7**,[5)] **8**,[6,7)] and **9**,[7)] have been investigated in some detail. We report here the experimental details of the syntheses of **4** (n = 2—4) and the results of X-ray diffraction analyses of these compounds.[8)] During the present study, the synthesis of **4b** (n = 2 for **4**) was reported by König et al.[9)]

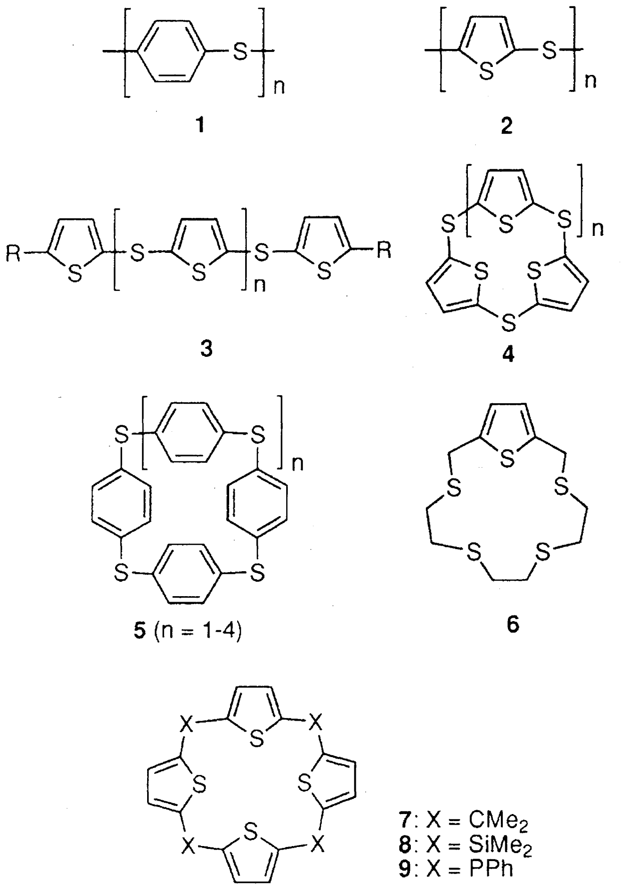
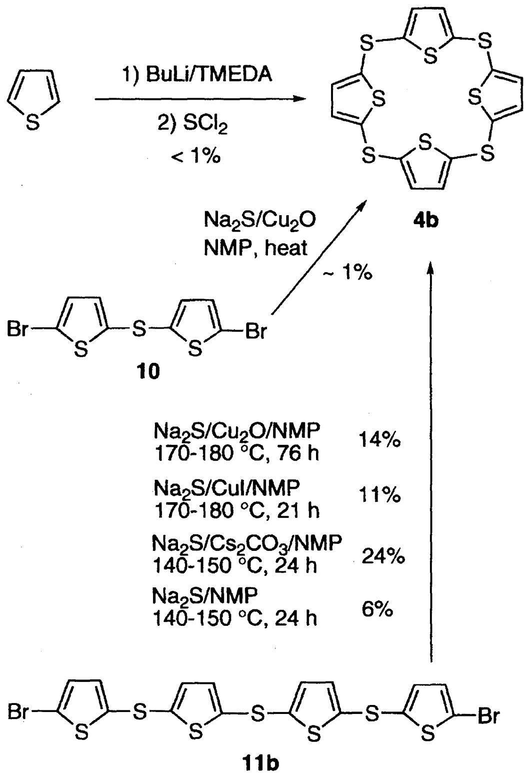


Chart 1.

Results and Discussion

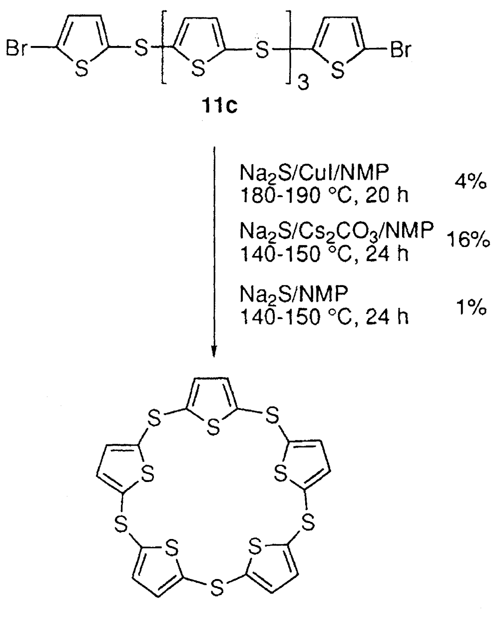
Synthesis. 1,7,13,19-Tetrathia[1.$_4$](2,5)thiophenophane (**4b**), which is composed of four thiophene rings and four sulfide linkages, was obtained in less than 1% yield by reaction of 2,5-dilithiothiophene with SCl_2 (Scheme 1).[9)] We have also tried the preparation of **4b** by heating the dibromide **10**[2)] with anhydrous Na_2S in the presence of Cu_2O[10)] in 1-methyl-2-pyrrolidinone (NMP). Prolonged heating of the mixture at 130—140 °C resulted in the complete consumption of **10**, but, disappointingly, gave a complex mixture from which **4b** was isolated only in about 1% yield. We therefore next examined its preparation from the dibromide **11b**[2)] under a variety of conditions. In every case, the reaction was carried out by using a dilute solution (0.1 M, 1 M = 1 mol dm^{-3}) of **11b** with a molar ratio of **11b** : Na_2S = 1 : 1. Thus, heating of **11b** and Na_2S in NMP in the presence of Cu_2O[10)] for 76 h at 170—180 °C gave **4b** in 14% yield. The use of CuI,[11)] instead of Cu_2O, gave **4b** in 11% yield with shortening of the reaction time (21 h). The use of Cs_2CO_3[12—14)] gave the best results. Thus, heating a mixture of **11b** and Na_2S in NMP in the presence of Cs_2CO_3 at 140—150 °C for 24 h afforded



Scheme 1.

4b in 24% yield. The benzene counterparts **5** of **4b** were satisfactorily prepared by mere heating of *p*-dihalobenzenes with Na$_2$S in NMP.[3d)] In the present case, however, simple heating of **11b** and Na$_2$S in NMP gave **4b** only in 6% yield.

1, 7, 13, 19, 25- Pentathia[1.$_5$](2, 5)thiophenophane (**4c**), which is composed of five –C$_4$H$_2$S–S– segments, was also prepared by reaction of the dibromide **11c**[2)] with Na$_2$S (Scheme 2). The conditions applied to the preparation of **4b** were used again. Also, in this case, the best yield (16%) was attained by use of Cs$_2$CO$_3$. Both non-catalyzed and CuI-catalyzed reactions gave **4c** in poor yields.



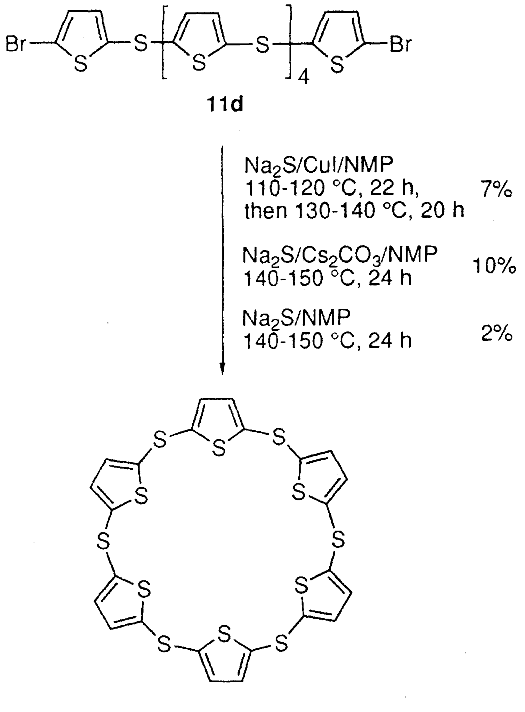
Scheme 2.

1,7,13,19,25,31-Hexathia[1.$_6$](2,5)thiophenophane (**4d**) is a typical macrocycle that has six C$_4$H$_2$S–S– units in its 24-membered ring. It was also most satisfactorily synthesized by the reaction of **11d**[2)] with Na$_2$S in the presence of Cs$_2$CO$_3$. Yields and conditions for the synthesis of **4d** are summarized in the Scheme 3.

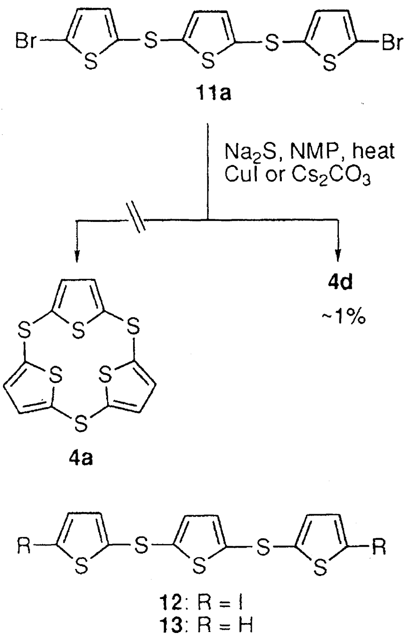
Attempts to prepare the smaller thiophenophane **4a** from **11a**[2)] and Na$_2$S, which is seemingly the most strained among this class of compounds, were all fruitless (Scheme 4). In these attempts, the compound **4d** was obtained only in a small amount. The use of the diiodide **12**, instead of **11a**, gave the reduction product **13** in good yield. Meanwhile, attempted preparation of a larger thiophenophane, for example, containing seven C$_4$H$_2$S–S– units, was hampered by the difficulty of obtaining the corresponding dibromide.

Structure. Thiophenophanes **4b**—**d** gave very simple ^{1}H and ^{13}C NMR spectra at 25 °C (Table 1). Every compound showed only one signal in the ^{1}H NMR in the narrow range of δ = 6.98—7.05 due to the β-hydrogens of the thiophene ring, and two signals in the ^{13}C NMR in the narrow ranges of δ = 138.0—140.4 and 132.2—133.4 due to the α- and β-carbons of the thiophene ring, respectively. Thus, all of the thiophene rings in these compounds are chemically equivalent, indicating conformational mobility in CDCl$_3$ at 25 °C.

Figure 1 shows UV-vis spectra of **4b**—**d** determined in CHCl$_3$. For the linear oligomers **3**, molar absorption coefficients (ε) and the longest absorption maxima ($\lambda_{\max}$) increase



Scheme 3.



Scheme 4.

Table 1. ^{1}H and ^{13}C NMR Chemical Shift Values (δ) of Thiophenophanes **4b**—**d** (at 25 °C in $CDCl_3$ with Me_4Si as Internal Standard)

	4b	**4c**	**4d**
β-H	6.98[a)]	7.05[a)]	7.02[b)]
α-C	140.4[c)]	138.5[c)]	138.0[c)]
β-C	132.2	133.4	132.9

a) 200 MHz. b) 400 MHz. c) 100.6 MHz.

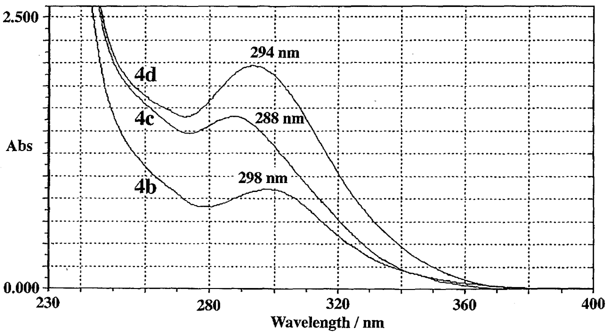


Fig. 1. UV-vis spectra of **4b**—**d** in $CHCl_3$.

progressively with an increasing number of the thiophene rings.[2)] In the present cyclic system, however, although ε values increase with an increasing number of the thiophene rings, λ_{max} values do not; 298 nm (ε 17700) for **4b**, 288 (30600) for **4c**, and 294 (39400) for **4d**. These results suggest that the conjugation between thiophene units through sulfide bonding takes place most effectively for **4b**, probably it has the most flexible conformation among these compounds. This conformational mobility might have exserted some influence on the yield of their synthesis; for example, the yield of **4b** (24%) was better than that of **4c** (14%) and **4d** (10%) for the synthesis in the presence of Cs_2CO_3.

After numerous attempts, single crystals of **4b**—**d**, suitable for X-ray diffraction analysis, were obtained on crystallization from chlorobenzene. Figure 2 shows a side view (left) and a top view (right) of the molecular structure of **4b**. For calix[4]arenes, four discrete forms exist; these are called cone, partial cone, 1,2-alternate, and 1,3-alternate conformations. If we presume the present compounds to be calixarenes, the side view reveals that **4b** adopts an 1,2-alternate conformation in the crystalline state just as the silicon counterpart **8** does.[6)] Non-bonded distances between the diagonal sulfur atoms of the thiophene rings are given in the top view to provide further information on the size of the cavity. Incidentally, all of the thiophene rings and sulfide bonds are normal in bond lengths and angles.

Figure 3 shows a side view (left) and a top view (right) of the molecular structure of **4c**. The conformation corresponds to the partial cone structure. Thus, the sulfur atoms of the four thiophene rings face upward, whereas that of the remaining one faces downward. Bond lengths and angles in the thiophene rings and sulfide bonds are normal also for this compound. Non-bonded distances (mean values of

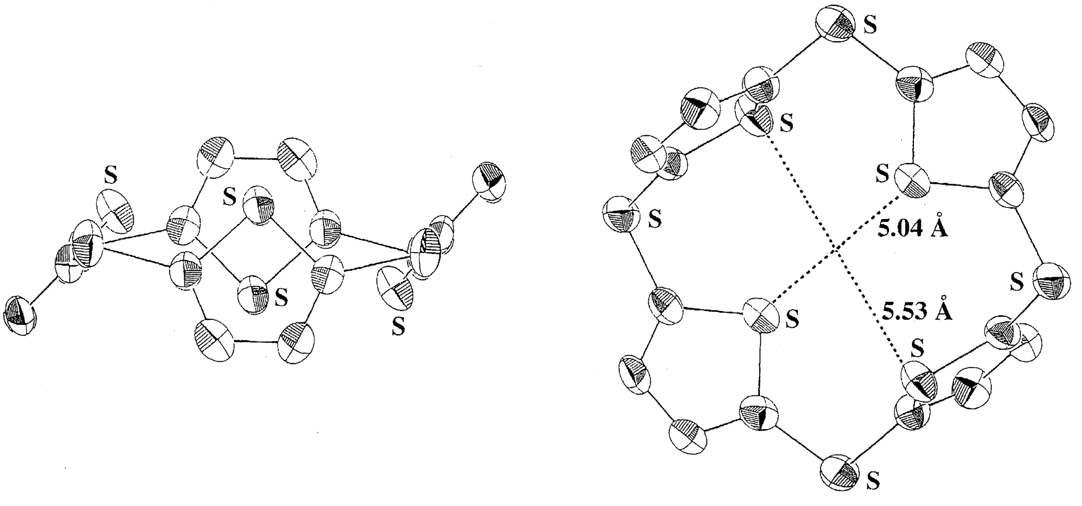


Fig. 2. Molecular structure of **4b**: Side view (left) and top view (right).

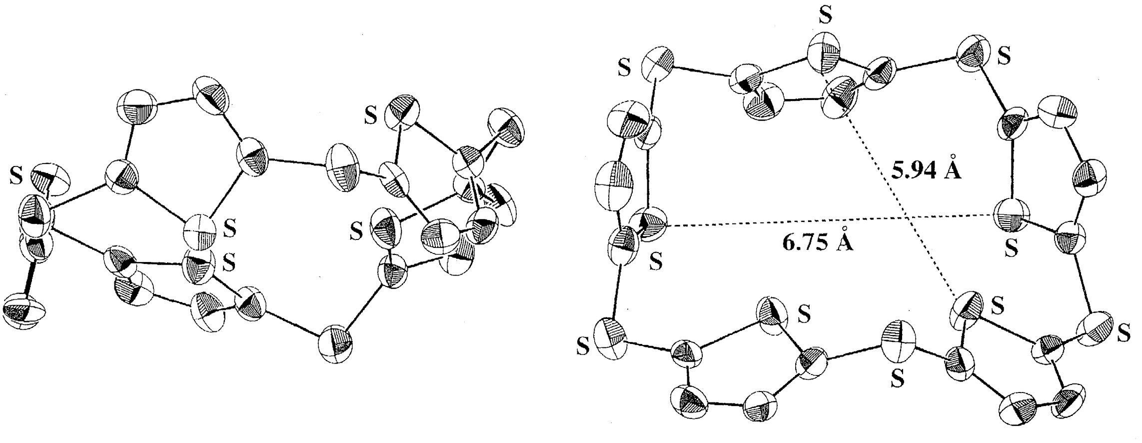


Fig. 3. Molecular structure of **4c**: Side view (left) and top view (right).

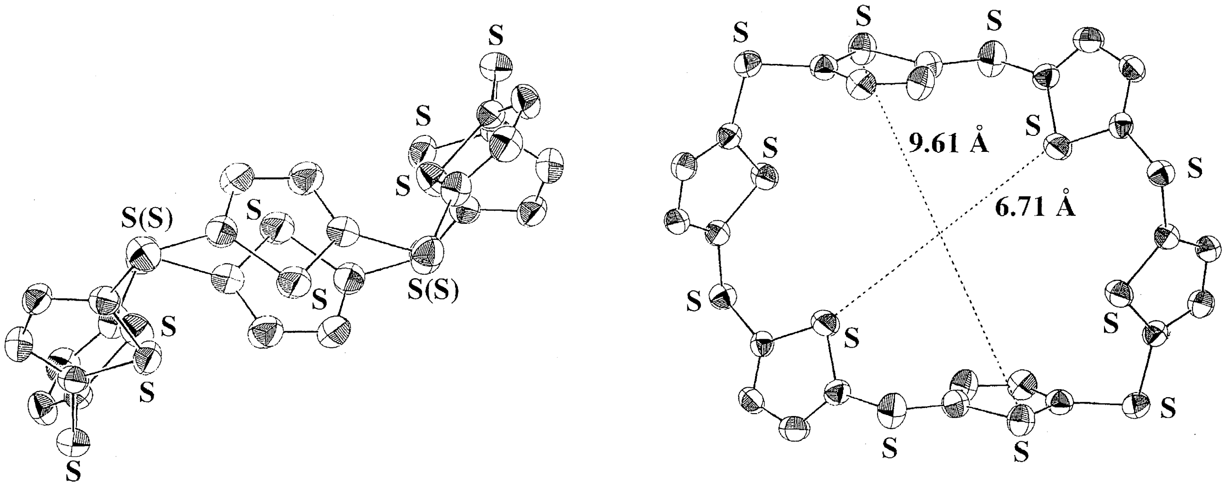


Fig. 4. Molecular structure of **4d**: Side view (left) and top view (right).

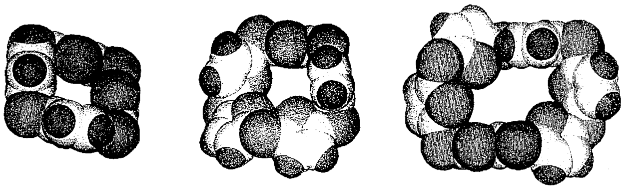


Fig. 5. Space-filling molecular models of **4b** (left), **4c** (center), and **4d** (right).

two molecules) between the diagonal sulfur atoms of the thiophene rings are also given in the top view to provide information on the size of the cavity.

Figure 4 shows a side view (left) and a top view (right) of the molecular structure of **4d**. As is evident from the side view, the six sulfur atoms of the sulfide bonds in this molecule are arranged to form the chair conformation of cyclohexane. Relevant non-bonded distances between the sulfur atoms, given in the top view, reveal that this macrocycle has a large cavity.

Figure 5 shows top views of space-filling molecular models of compounds **4b**—**d**. They show that these compounds possess a sharp-cut cavity and resemble a doughnut rather than a calix crater. Thus, they, as a host, would be capable of accepting a guest not only from the top side but also from the bottom side.

Experimental

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400, a Bruker ARX-400, or a Bruker AC-200 spectrometer with tetramethylsilane (δ = 0.0 for ^{1}H) and $CDCl_3$ (δ = 77.0 for ^{13}C) as the internal standard. UV-vis spectra were determined on a Shimadzu UV-160A spectrophotometer. Mass spectra (EI) were determined on a JEOL DX-303 spectrometer. Merck 7734 Kiesel Gel (70—230 mesh ASTM) was used for silica-gel column chromatography. Gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908. Cu_2O[15] and CuI[16] were prepared according to the literature methods. Anhydrous Na_2S (Aldrich) was used as purchased. Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

Preparation of 1,7,13,19-Tetrathia[1.₄](2,5)thiophenophane (4b). a) In the Presence of Cu_2O. A mixture of 1.17 g (2 mmol) of **11b**,[2] 156 mg (2 mmol) of anhydrous Na_2S, and 33 mg (0.2 mmol) of Cu_2O in 200 ml of 1-methyl-2-pyrrolidinone (NMP) was carefully deaerated and heated at 170—180 °C for 76 h under argon. The NMP was distilled under reduced pressure. The residue was heated with 200 ml of benzene for 1.5 h. The mixture was filtered while hot. The filtrate was evaporated and the residue was chromatographed on a column of silica gel. The column was eluted with cyclohexane to give 131 mg (14%) of **4b**: Mp 242.0—243.5

°C [lit,[9] mp 200 °C (decomp)]; nearly colorless crystals (from chloroform); MS *m/z* 456 (M$^+$). Found: C, 42.05; H, 1.68%. Anal. Calcd for $C_{16}H_8S_8$: C, 42.07; H, 1.76%.

b) In the Presence of CuI. A mixture of 1.17 g (2 mmol) of **11b**, 156 mg (2 mmol) of anhydrous Na_2S, and 39 mg (0.2 mmol) of CuI in 200 ml of NMP was deaerated and heated at 170—180 °C for 21 h under argon. The resulting mixture was treated in the same manner as described above to give 96 mg (11%) of **4b**.

c) In the Presence of Cs_2CO_3. A mixture of 587 mg (1 mmol) of **11b**, 78 mg (1 mmol) of anhydrous Na_2S, and 326 mg (1 mmol) of Cs_2CO_3 in 100 ml of NMP was heated at 140—150 °C for 22 h under argon. The resulting mixture was treated in the same manner as described above to give 109 mg (24%) of **4b**.

d) In the Absence of Additive. A mixture of 585 mg (1 mmol) of **11b** and 79 mg (1 mmol) of anhydrous Na_2S in 100 ml of NMP was heated at 140—150 °C for 24 h under argon. The resulting mixture was treated in the same manner as described above to give 28 mg (6%) of **4b**.

Preparation of 1,7,13,19,25-Pentathia[1.$_5$](2,5)thiophenophane (4c). **a) In the Presence of CuI.** A mixture of 699 mg (1 mmol) of **11c**,[2] 81 mg (1 mmol) of anhydrous Na_2S, and 40 mg (0.1 mmol) of CuI in 200 ml of NMP was heated at 180—190 °C for 20 h under argon. The resulting mixture was treated in the same manner as described above to give 24 mg (4%) of **4c**: Mp 196—197 °C; colorless feathery crystals (from cyclohexane); MS *m/z* 570 (M$^+$). Found: C, 42.32; H, 1.75%. Anal. Calcd for $C_{20}H_{10}S_{10}$: C, 42.07; H, 1.76%.

b) In the Presence of Cs_2CO_3. A mixture of 701 mg (1 mmol) of **11b**, 79 mg (1 mmol) of anhydrous Na_2S, and 328 mg (1 mmol) of Cs_2CO_3 in 100 ml of NMP was heated at 140—150 °C for 24 h under argon. The resulting mixture was treated in the same manner as described above to give 92 mg (16%) of **4c**.

c) In the Absence of Additive. A mixture of 701 mg (1 mmol) of **11b** and 79 mg (1 mmol) of anhydrous Na_2S in 100 ml of NMP was heated at 140—150 °C for 24 h under argon. The resulting mixture was treated in the same manner as described above to give 34 mg (6%) of **4b**.

Preparation of 1,7,13,19,25,31-Hexathia[1.$_6$](2,5)thiophenophane (4d). **a) In the Presence of CuI.** A mixture of 813 mg (1 mmol) of **11d**,[2] 80 mg (1 mmol) of anhydrous Na_2S, and 20 mg (0.2 mmol) of CuI in 200 ml of NMP was heated at 110—120 °C for 22 h and then at 130—140 °C for 20 h under argon. The NMP was distilled under reduced pressure. The residue was heated with 200 ml of benzene for 1.5 h. The mixture was filtered while hot and the filtrate was evaporated. Purification of the residue by silica-gel column chromatography (with cyclohexane as the eluent), followed by purification by GPC, gave 47 mg (7%) of **4d**: Mp 234—235 °C; faint-pale yellow needles (from chlorobenzene); MS *m/z* 684 (M$^+$). Found: C, 42.05; H, 1.68%. Anal. Calcd for $C_{16}H_8S_8$: C, 42.07; H, 1.76%.

b) In the Presence of Cs_2CO_3. A mixture of 813 mg (1 mmol) of **11d**, 78 mg (1 mmol) of anhydrous Na_2S, and 326 mg (0.1 mmol) of Cs_2CO_3 in 100 ml of NMP was heated at 140—150 °C for 26 h under argon. The resulting mixture was treated in the same manner as described above to give 67 mg (10%) of **4c**.

c) In the Absence of Additive. A mixture of 813 g (1 mmol) of **11c** and 78 mg (1 mmol) of anhydrous Na_2S in 100 ml of NMP was heated at 140—150 °C for 25 h under argon. The resulting mixture was treated in the same manner as described above to give 14 mg (2%) of **4d**.

Attempted Preparation of 1,7,13-trithia[1.$_3$](2,5)thiophenophane (4a). **a) From 11a and Na_2S.** A mixture of 471 mg (1 mmol) of **11a**,[2] 78 mg (1 mmol) of Na_2S, and 326 mg (1 mmol) of Cs_2CO_3 in 100 ml of NMP was heated at 140—150 °C for 23 h under argon. Purification of the mixture by silica-gel column chromatography and then by GPC gave 1.5 mg (0.4%) of **4d**. No expected **4a** was isolated.

b) From 12 and Na_2S. A mixture of 565 mg (1 mmol) of **12**, 78 mg (1 mmol) of Na_2S, and 326 mg (1 mmol) of Cs_2CO_3 in 100 ml of NMP was heated at 140—150 °C for 3 h under nitrogen.

Table 2. Crystal Data of **4b**—**d**

	4b	**4c**	**4d**
Chemical formula	$C_{16}H_8S_8$	$C_{20}H_{10}S_{10}$	$C_{24}H_{12}S_{12}$
Formula weight	456.77	570.96	685.15
Crystal color	Colorless	Colorless	Faint-brown
Crystal form	Plates	Needles	Needles
Crystal size/mm^3	0.16 × 0.13 × 0.03	0.40 × 0.08 × 0.04	0.32 × 0.04 × 0.03
Unit-cell dimensions			
a/Å	7.623(2)	6.0440(7)	5.670(1)
b/Å	6.347(2)	17.025(3)	9.169(3)
c/Å	18.658(4)	22.726(4)	13.598(3)
α/°		90.003(8)	98.44(1)
β/°	96.82(1)	90.014(8)	90.59(1)
γ/°		85.967(9)	104.38(1)
V/Å^3	896.3(4)	2332.7(7)	676.6(3)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Z	2	4	1
D_c/Mg m^{-3}	1.692	1.626	1.681
No. of observed reflections	2285	10123	2982
No. of independent reflections	1858	8246	1506
R	0.049	0.047	0.046
R_w	0.056	0.049	0.053
GOF	1.545	1.968	1.360

Purification of the mixture by silica-gel column chromatography gave 286 mg (91%) of **13**. The use of CuI, instead of Cs_2CO_3, gave **13** in 29% yield.

The diiodide **12** was prepared from **13** in the following way. To a solution of 3.13 g (10 mmol) of **13** in a mixture of 50 ml of $CHCl_3$ and 25 ml of AcOH was added 4.51 g (20 mmol) of *N*-iodosuccinimide in small portions at 0 °C. After being stirred for 3 h at 0 °C, the mixture was diluted with $CHCl_3$, washed successively with water, aqueous $NaHCO_3$, and water, dried, and evaporated. The residue was recrystallized from hexane to give 2.76 g (49%) of **12**: Mp 74—75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.86$ (d, $J = 4$ Hz, 4H), 6.98 (s, 2H), 7.10 (d, $J = 4$ Hz, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) $\delta = 77.6$, 132.5, 134.9, 137.5, 138.9, 139.1. Found: C, 25.70; H, 1.07%. Anal. Calcd for $C_{12}H_6I_2S_5$: C, 25.54; H, 1.07%.

X-Ray Structural Analysis of 4b—d. Crystal data are given in Table 2. The data were recorded on a Mac Science DIP3000 diffractometer equipped with a graphite monochrometer. Oscillation and nonscreen Weissenberg photographs were recorded on the imaging plates of the diffractometer by using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and the data reduction was made by the MAC DENZO program system. Cell parameters were determined and refined by using the MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR in the CRYSTAN-GM program system. The atomic coordinates and anisotropic thermal parameters of the non-H atoms were refined by full-matrix least squares.

The complete $F_o - F_c$ data together with relevant data including bond distances and angles have been deposited as Document 71052 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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