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Synthesis of Sulfur-containing Large-membered Heterocycles (Crown Thioethers) with Bis(*o*-mercapto)phenyl Sulfide

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Abstract Bis(*o*-mercaptophenyl) sulfide (**4**) condensed with 1,2-dibromoethane in the presence of Cs_2CO_3 in DMF to give the 9-membered-ring 1:1-condensation product (**9**), the 18-membered ring 2:2 condensation product (**10**), and the 27-membered ring 3:3 condensation product (**11**) in 42, 19, and 5% yields, respectively. The condensation of **4** with 1,3-dibromopropane gave the 10-membered ring 1:1 condensation product (**12**) as the sole identifiable product in 42% yield. The reaction of **4** with *cis*-1,2-dichloroethylene in refluxing EtOH in the presence of EtONa provided the two isomeric 1:1-condensation products (**14**) (25%) and (**15**) (5%) along with the 2:2 condensation product (**16**) (20%). X-Ray crystallographic analyses of **10**, **14**, and **15** are also reported.

Keywords *Ring closure, sulfides, S-containing heterocycles, large-membered ring, crown thioethers, X-ray crystallographic analysis*

Recently we have devised a convenient one-pot synthesis of a polycyclic sulfonium salt, 9a*H*-9,10-dithia-4b-thioniaindeno[1,2-*a*]indene chloride (**3**), which involves the reaction of ethylene trithiocarbonate (**1**) with benzyne, generated by thermolysis of two molar amounts of 2-carboxybenzenediazonium chloride (**2**).[1,2] Heating the sulfonium salt (**3**) in refluxing methanol provided an easy access to bis(*o*-mercaptophenyl) sulfide (**4**),[3] which otherwise seems to be difficult to synthesize in a preparative scale.[4] The condensations of the dithiol **4** with formaldehyde and diiodomethane gave a 1:1 condensation product **5** and/or a 2:2 condensation product **6**, whereas the condensations with 1,1'-carbonyl- and 1,1'-thiocarbonyldiimidazoles provided only 2:2 condensation products **7** and **8**, respectively.[5] In the extention of this study, we have now investigated the condensation of **4** with some reagents which possess a two- or three-carbon unit with expectation of obtaining sulfur-containing large-membered heterocyclic compounds (crown thioethers).[6]

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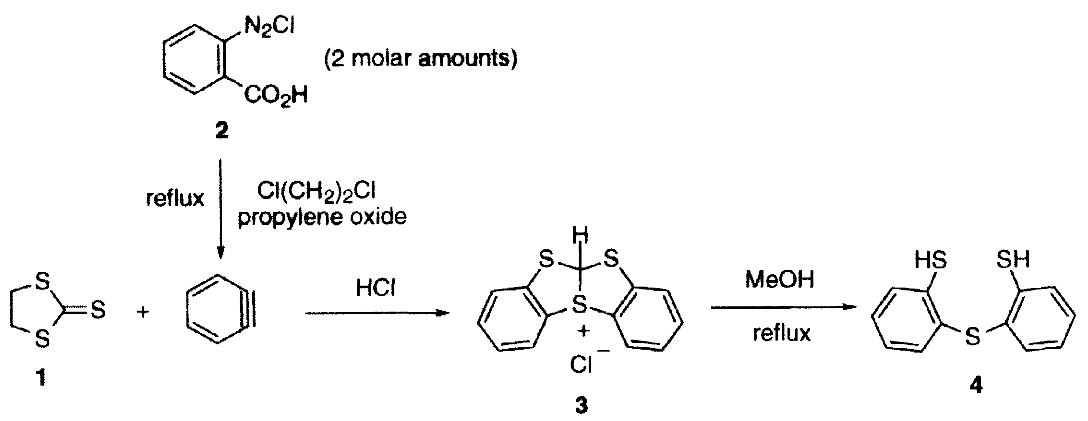

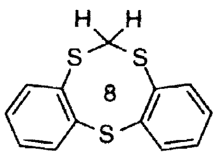

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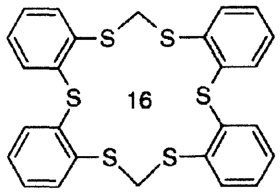

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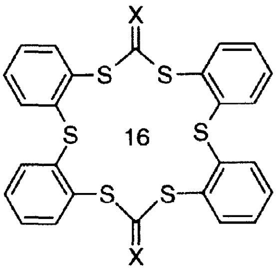


7: X = O, **8**: X = S

RESULTS AND DISCUSSION

Condensation of the Dithiol (4) with 1,2-Dibromoethane

The condensation was carried out in *N*,*N*-dimethylformamide (DMF) or tetrahydrofuran (THF) in the presence of Cs_2CO_3[7] under a variety of concentrations of the reactants (Table1). The best results were obtained in the following way. Solutions of **4** (1.0 mmol) and 1,2-dibromoethane (1.0 mmol) in each 10 ml of DMF were added simultaneously to a stirred suspension of Cs_2CO_3 (1.1 mmol) in 30 ml of DMF over a period of 1 h, and then the mixture was stirred for 24 h (run 3). Purification of the mixture by silica-gel column chromatography followed by gel permeation chromatography (GPC) gave the 1:1-condesation product (**9**), the 2:2 condensation product (**10**), and the 3:3 condensation product (**11**) in 42, 19, and 5% yields, respectively. These three compounds, which have never been synthesized previously, are benzo-annelated perthia derivatives of 9-crown-3-, 18-crown-6-, and 24-crown-9-ethers, respectively. ^1H NMR spectra of all of these compounds showed only one singlet due to the methylene hydrogens and multiplets due to the aromatic hydrogens, and ^{13}C NMR spectra showed only one peak due to the methylene carbons and six peaks due to the aromatic carbons. MS spectra of **9**, **10**, and **11** gave the molecular ion peaks at the correct positions of *m/z* 276, 552, and 828, respectively. The structure of **10** was also confirmed by an X-ray crystallographic analysis as described later.

The condensation also, in many cases, gave some acyclic bromine-containing by-products whose structures were not determined.

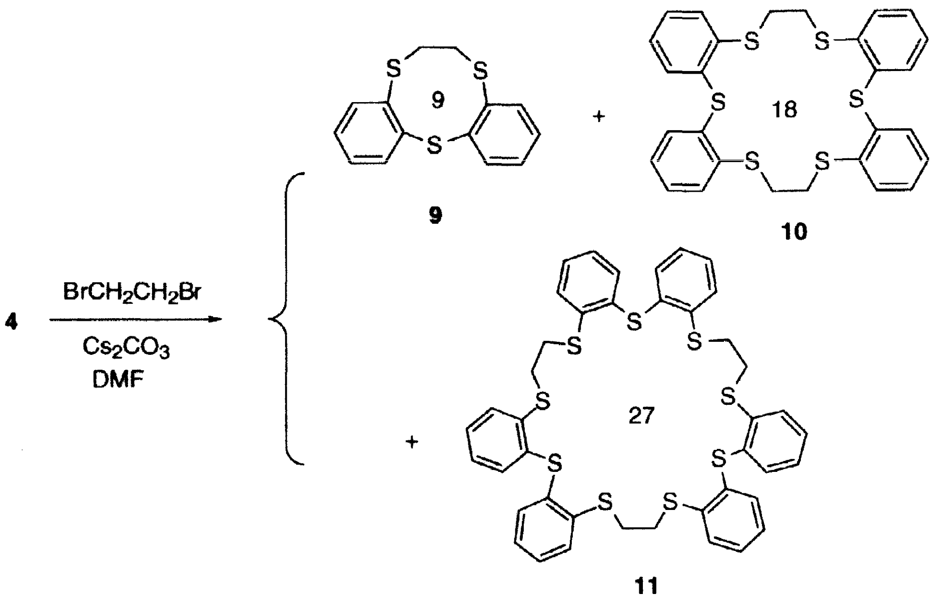


Table 1. Condensation of the dithiol (**4**) with 1,2-dibromoethane under a variety of conditions

runs	Products (%)		
	9	**10**	**11**
1[a]	6	15	4
2[b]	20	17	4
3[c]	42	19	5
4[d]	38	19	5
5[e]	2	6	0

[a] A mixture of **4** (1.0 mmol), 1,2-dibromoethane (1.0 mmol), and Cs_2CO_3 (1.1 mmol) in 20 ml of DMF was stirred.

[b] To a stirred suspenison of Cs_2CO_3 (1.1 mmol) in 10 ml of DMF were added simultaneously **4** (1.0 mmol) and 1,2-dibromoethane (1.0 mmol) each dissolved in 10 ml of DMF.

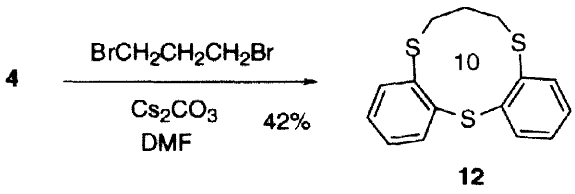
[c] To a stirred suspenison of Cs_2CO_3 (1.1 mmol) in 30 ml of DMF were added simultaneously **4** (1.0 mmol) and 1,2-dibromoethane (1.0 mmol) each dissolved in 10 ml of DMF.

[d] To a stirred suspenison of Cs_2CO_3 (1.1 mmol) in 50 ml of DMF were added simulataneously **4** (1.0 mmol) and 1,2-dibromoethane (1.0 mmol) each dissolved in 10 ml of DMF.

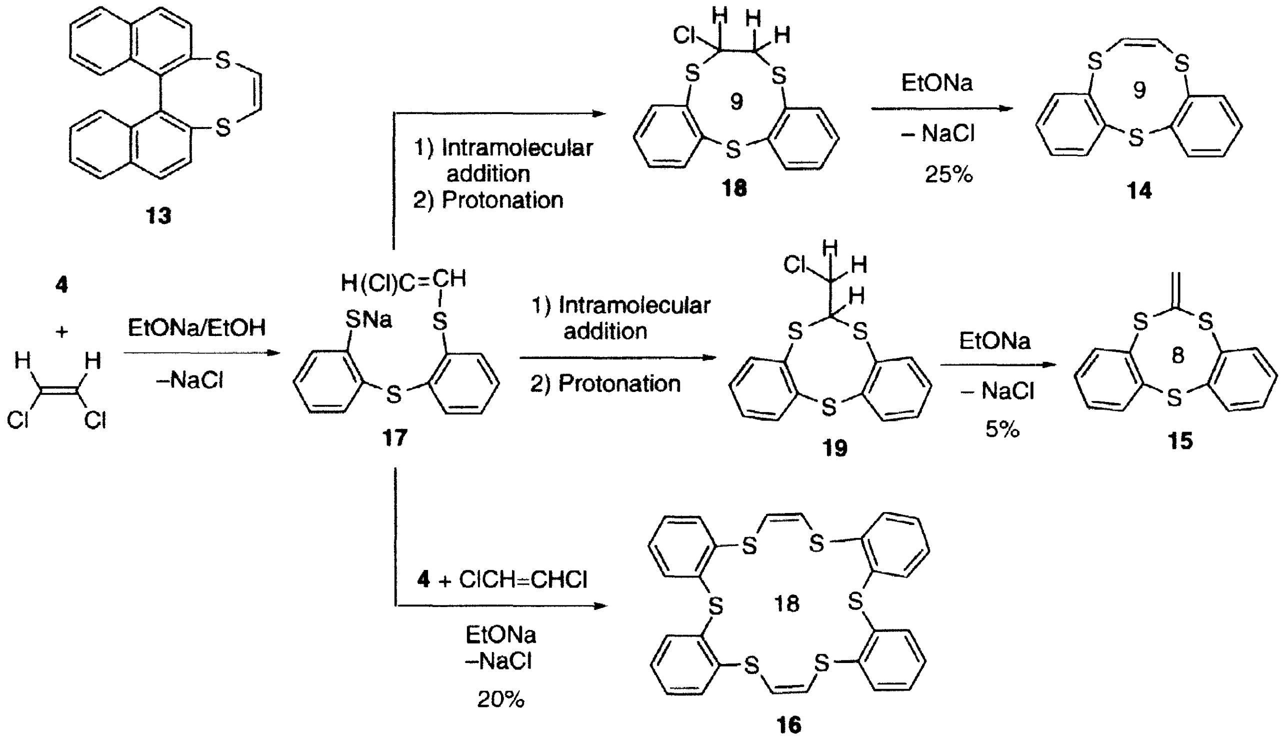
[e] To a stirred suspenison of Cs_2CO_3 (1.1 mmol) in 10 ml of THF were added simultaneously **4** (1.0 mmol) and 1,2-dibromoethane (1.0 mmol) each dissolved in 10 ml of THF.

Condensation of the Dithiol (4) with 1,3-Dibromopropane

The condensation was examined under a range of concentrations of the reactants. The best yield (42%) of the expected product (**12**) was attained by simultaneous addition of **4** (1.0 mmol) and 1,3-dibromopropane (1.0 mmol), each dissolved in 10 ml of DMF, to a stirred suspension of Cs_2CO_3 (1.1 mmol) in 70 ml of DMF. Other larger-ring compounds could not be isolated in pure form in this condensation.



Condensation of the Dithiol (4) with *cis*-1,2-Dichloroethylene



The condensation was carried out by heating a dilute solution of the dithiol **4** (1.0 mmol), *cis*-1,2-dichloroethylene (1.0 mmol), and sodium ethoxide (2.6 mmol) in ethanol (100 ml) under reflux. The reaction in a more concentrated solution gave less satisfactory results. The reaction, done in this way, resulted in the separation of a white powder which is hardly soluble in ordinary organic solvents at room temperature. Crystallization of the powder from chlorobenzene gave colorless crystals of the 18-membered 2:2 condensation product (**16**) in 20% yield. The compound **16** showed the correct molecular ion peak at *m/z* 548 in the MS spectrum. Purification of the filtrate of the original reaction mixture by alumina column chromatography provided the two isomeric 1:1 condensation products (**14**) and (**15**) in 25 and 5% yields, respectively. These two compounds, which were not separable by GPC indicating that their molecular weights are similar to each other, showed the correct parent peaks as the 1:1 condensation product in the Mass spectra. Their structural difference is most clearly reflected in the ^{13}C NMR spectra: the major isomer **14** showed seven sp^2 carbon peaks (one alkenic + six aromatic carbons), whereas the minor isomer eight sp^2 carbon peaks (two alkenic + six aromatic carbons). In the ^{1}H NMR spectra, the exo-methylene hydrogens of **15** and the alkenic hydrogens of **14** appeared at δ 5.98 and 6.48, respectively, as a singlet, the chemical shift values which do not contradict the assigned structures. Further, the structure of these compounds was confirmed by X-ray crystallographic analyses.

To our knowledge, only a limited number of unsaturated crown thioethers, containing more than nine members, have been synthesized.[6] Reportedly, the condensation of 1,1'-binaphthalene-2,2'-dithiol with *cis*-1,2-dichloroethylene provided the eight-membered ring compound **13** in high yield under conditions similar to those described above, and neither the 2:2 condensation procut nor the exo-methylene compound corresponding to **15** was formed.[8] In the present case, the intermediate **17** may resist cyclization to the nine-membered ring **18** probably because of unfavorable geometric demand of the cyclization transition state. The cyclization is therefore accompanied both by cyclization to the eight-membered ring **19** and by further reaction with **4** and *cis*-1,2-dichloroethylene that leads to the 2:2 condensation product **16**. The base-catalyzed dehydrobromination of **18** and **19** would provide **14** and **15**, respectively, as the final products.

X-Ray Crystallographic Analyses of Compounds 10, 14, and 15

Molecular structures of **10**, **14**, and **15** are given in Figures 1, 2, and 3, respectively, along with the relevant bond lengths, bond angles, and torsion angles data. X-Ray crystallographic data of these compounds are summarized in Table 2.

The X-ray crystallographic analysis of the compound **10** disclosed that two conformationally independent molecules exist in a unit cell, which are shown in Figure 1. Although the methylene carbons in the both molecules are conformationally nonequivalent in the crystals, the ^{1}H NMR spectrum, which showed only one singlet due to the methylene hydrogen atoms, is indicative of the flexibility of the ring structure in solution. No extreme deviation was observed in the bond lengths and the bond angles compared to those of the common alkyl phenyl sulfides. The C(sp^2)-S bond lengths (1.759-1.777 Å) are slightly shorter than the C(sp^3)-S bond lengths (1.808-1.825 Å). The molecule possesses a sizable hole and thus will serve as the host for many soft electrophiles.

The X-ray crystallographic analysis established the *cis*-structure of the compound **14**. Although the ^{1}H NMR spectrum exhibited only one singlet due to the vinylene hydrogen atoms indicating the mobility of the ring structure, the two vinylene carbons, two benzene rings, and three sulfur atoms are nonequivalent in the crystalline state. No extreme deviation was observed in the bond lengths and the bond angles data. A rather unexpected feature is the shortening of the C(5)-C(9) double bond length, 1.309 Å.

The *exo*-methylene structure of the compound **15** was determined by the X-ray crystallographic analysis (Figure 3). Any axis, plane, or point of symmetry does not exist in the molecule in the crystalline state, although the two benzene rings and two *exo*-methylene hydrogen atoms are equivalent in solution as is evident from the ^{1}H NMR spectrum.

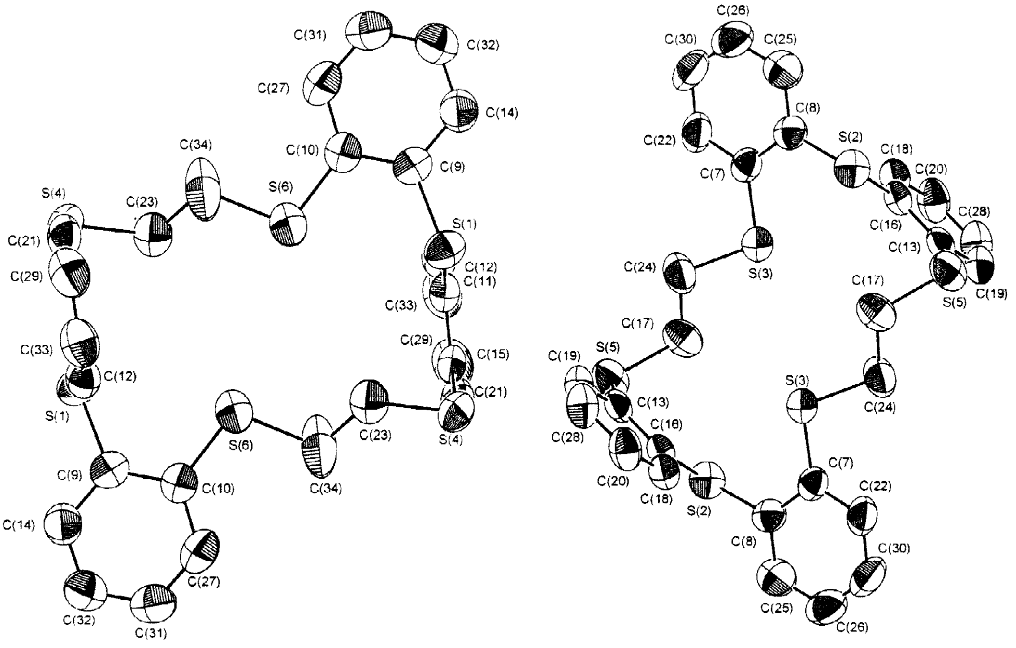
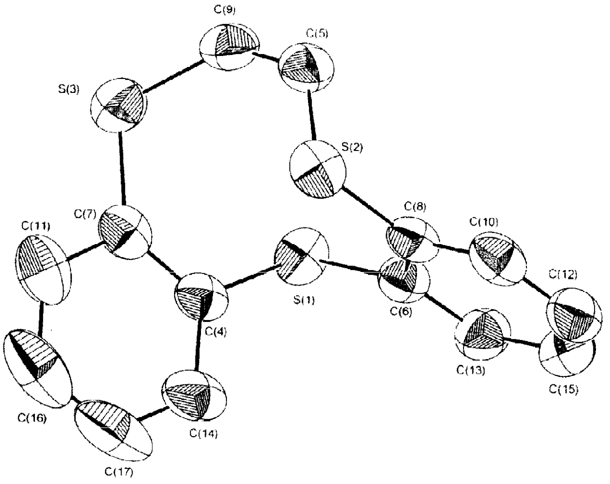


Figure 1. Molecular structures of two independent molecules of **10** (thermal ellipsoids at non-hydrogen atoms are at 50% probability and the numbering in the figure does not correspond to the nomenclature). Relevant bond lengths (Å), bond angles (deg), and torsion angles (deg) data. Left-hand molecule: S(1)-C(9), 1.774(3); S(1)-C(11), 1.768(3); S(4)-C(15), 1.777(3); S(6)-C(10), 1.759(3); S(4)-C(23), 1.824(4); S(6)-C(34), 1.808(5). C(9)-S(1)-C(11), 104.5(2); C(15)-S(4)-C(23), 101.2(2); C(10)-S(6)-C(34), 104.2(2). S(1)-C(10)-C(15)-S(4), 3.5(2); S(1)-C(9)-C(10)-S(6), 11.2(2); S(4)-C(23)-C(34)-S(6), –159.7(4). Right-hand molecule: S(2)-C(8), 1.770(3); S(2)-C(16), 1.774(3); S(3)-C(7), 1.764(3); S(5)-C(13), 1.771(4); S(3)-C(24), 1.810(4); S(5)-C(17), 1.825(4). C(8)-S(2)-C(16), 104.0(2); C(7)-S(2)-C(16), 102.9(2); C(13)-S(5)-C(17), 101.0(2). S(3)-C(7)-C(8)-S(2), –7.7(2); S(5)-C(13)-C(16)-S(2), 0.4(2); S(5)-C(17)-C(24)-S(3), –169.5(4).

Figure 2. Molecular structure of **14** (thermal ellipsoids at non-hydrogen atoms are at 50% probability and the numbering in the figure does not correspond to the nomenclature). Relevant bond lengths (Å), bond angles (deg), and torsion angles (deg) data: C(5)-C(9), 1.309(5); S(1)-C(4), 1.769(3); S(1)-C(6), 1.768(3); S(2)-C(8), 1.781(3); S(3)-C(7), 1.773(3); S(2)-C(5), 1.763(3); S(3)-C(9), 1.732(3). C(4)-S(1)-C(6), 101.7(2); C(5)-S(2)-C(8), 101.8(2); C(7)-S(3)-C(9), 109.9(2). S(1)-C(6)-C(8)-S(2), 5.3(2); S(1)-C(4)-C(7)-S(3), –0.4(2); S(2)-C(5)-C(9)-S(3), –6.5(2).



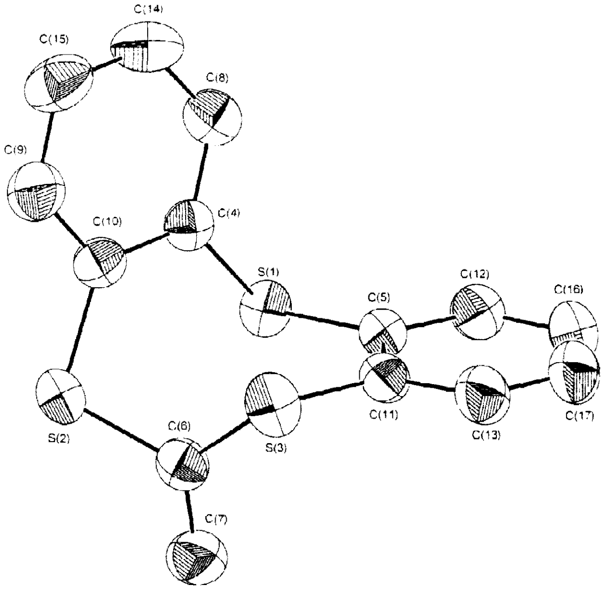


Figure 3. Molecular structure of **15** (thermal ellipsoids at non-hydrogen atoms are at 50% probability and the numbering in the figure does not correspond to the nomenclature). Relevant bond lengths (Å), bond angles (deg), and torsion angles (deg) data: C(6)-C(7), 1.311 (4); S(1)-C(4), 1.777(2); S(1)-C(5), 1.775(2); S(2)-C(10), 1.764(2); S(3)-C(11), 1.763(2); S(2)-C(6), 1.764(2); S(3)-C(6), 1.771(3). C(4)-S(1)-C(5), 104.0(1); C(6)-S(2)-C(10), 103.4(1); C(6)-S(3)-C(11), 103.8(1); S(2)-C(6)-S(3), 116.5(2). S(1)-C(4)-C(10)-S(2), 6.4(2); S(1)-C(5)-C(11)-S(3), -7.4(2).

Table 2. X-Ray crystallographic data of compounds **10**, **14**, and **15**

	10	**14**	**15**
Chemical formula	$C_{28}H_{24}S_6$	$C_{14}H_{10}S_3$	$C_{14}H_{10}S_3$
Formula weight	552.89	274.43	274.43
Crystal color	Colorless	Colorless	Colorless
Crystal form	Needles	Blocks	Needles
Crystal size/mm^3	0.35×0.12×0.10	0.20×0.14×0.12	0.36×0.12×0.10
Unit-cell dimensions			
a/Å	15.986(2)	8.300(1)	8.010(1)
b/Å	8.2700(4)	7.232(1)	20.995(3)
c/Å	20.504(2)	21.101(3)	8.075(1)
β/°	104.860(5)	93.931(8)	110.147(9)
V/Å^3	2620.1(4)	1263.6(3)	1274.9(3)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
Z	4	4	4
D_c/Mg m^{-3}	1.401	1.442	1.430
No. of observed reflections[a]	3669	2000	2151
No. of independent reflections	5928	3238	3172
No. of parameters varied	389	194	194
R	0.055	0.052	0.049
R_w	0.056	0.052	0.048
GOF	1.697	1.270	1.175

[a] $I > 2\sigma(I)$.

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EXPERIMENTAL

Melting points were determined on a MEL-TEMP capillary tube apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were determined on a Bruker AM400, a Bruker ARX400, and a Bruker AC300P spectrometer using $CDCl_3$ or DMSO-d_6 as the solvent with TMS as the internal standard (400, 400, and 300 MHz for ^{1}H and 100.6, 100.6, and 75.5 MHz for ^{13}C, respectively). MS spectra were obtained at 70 eV in the EI mode on a JEOL JMS-DX303 spectrometer. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. All of the reactions were carried out under argon. Silica-gel column chromatography was performed on Merck silica gel (7734, 70-230 mesh) and alumina column chromatography on Merck aluminum oxide 90 (70-120 mesh). GPC was performed on a Japan Analytical Industry LC-908.

Condensation of the Dithiol (4) with 1,2-Dibromoethane under a Variety of Conditions

a) A mixture of 250 mg (1.0 mmol) of **4**, 188 mg (1.0 mmol) of 1,2-dibromoethane, and 360 mg (1.1 mmol) of Cs_2CO_3 in 20 ml of DMF was stirred for 3 h at room temperature. The mixture was diluted with ice-water and extracted with CH_2Cl_2 (200 ml x 2). The combined extracts were washed with water, dried over $MgSO_4$, and evaporated. The resulting residue was chromatographed on a column of silica gel (60 g). The column was eluted with a mixture of hexane and CH_2Cl_2 (1:1) to give 120 mg of a mixture containing **9** and **10** and 48 mg of a mixture containing **10** and **11**. The former mixture was further purified by GPC to give 16 mg (6%) of **9** and 36 mg (13%) of **10**. The latter mixture was also purified by GPC to give 7 mg (3%) of **10** and 12 mg (4%) of **11**.

b) To a stirred suspension of 360 mg (1.1 mmol) of Cs_2CO_3 in 10 ml of DMF were added simultaneously solutions of 250 mg (1.0 mmol) of **4** in 10 ml of DMF and 188 mg (1.0 mmol) of 1,2-dibromoethane in 10 ml of DMF at room temperature. The mixture was stirred for 3 h. The resulting mixture was purified as described above to provide 54 mg (20%) of **9**, 46 mg (17%) of **10**, and 10 mg (4%) of **11**.

c) To a stirred suspension of 360 mg (1.1 mmol) of Cs_2CO_3 in 30 ml of DMF were added simultaneously solutions of 250 mg (1.0 mmol) of **4** in 10 ml of DMF and 188 mg (1.0 mmol) of 1,2-dibromoethane in 10 ml of DMF over a period of 1 h at room temperature. The mixture was stirred for 24 h. The resulting mixture was purified as described above to give 117 mg (42%) of **9**, 53 mg (19%) of **10**, and 15 mg (5%) of **11**.

d) To a stirred suspension of 360 mg (1.1 mmol) of Cs_2CO_3 in 50 ml of DMF were added simultaneously solutions of 250 mg (1 mmol) of **4** in 10 ml of DMF and 188 mg (1.0 mmol) of 1,2-dibromoethane in 10 ml of DMF over a period of 1 h at room temperature. The mixture was stirred for 24 h. The resulting mixture was purified as described above to give 104 mg (38%) of **9**, 53 mg (19%) of **10**, and 15 mg (5%) of **11**.

e) To a stirred suspension of 360 mg (1.1 mmol) of Cs_2CO_3 in 10 ml of THF were added simultaneously solutions of 250 mg (1.0 mmol) of **4** in 10 ml of THF and 188 mg (1.0 mmol) of 1,2-dibromoethane in 10 ml of THF over a period of 1 h at room temperature. The mixture was stirred for 5 h. The resulting mixture was purified as described above to give 4 mg (2%) of **9** and 16 mg (6%) of **10**.

2,3-Dihydrodibenzo[*e,h*][1,4,7]trithionin (9): mp 116.0-116.5 °C (from cyclohexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (4H, s, CH_2), 7.21-7.30 (4H, m), 7.61-7.64 (2H, m), 7.72-7.74 (2H, m); ^{13}C

NMR (100.6 MHz, $CDCl_3$) δ 36.0 (CH_2), 129.2, 129.6, 135.7, 137.1, 138.7, 142.2; MS *m/z* 276 (M^+), 216 (100%), 184, 167. Anal. Calcd for $C_{14}H_{12}S_3$: C, 60.83; H, 4.38. Found: C, 60.98; H, 4.34.

2,3:5,6:11,12:14,15-Tetrabenzo-1,4,7,10,13,16-hexathiacyclooctadeca-2,5,11,14-tetraene (10): mp 198.0-198.5 °C (from cyclohexane); ^1H NMR (400 MHz, $CDCl_3$) δ 3.17 (8H, s, CH_2), 7.08-7.10 (4H, m), 7.15-7.23 (8H, m), 7.49-7.52 (4H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 33.8 (CH_2), 127.6 128.3, 131.7, 134.0, 135.1, 139.2; MS *m/z* 552 (M^+), 248, 216 (100%), 184. Anal. Calcd for $C_{28}H_{24}S_6$: C, 60.83; H, 4.38. Found: C, 60.94; H, 4.28.

2,3,:5,6:11,12:14,15:20,21:23,24-Hexabenzo-1,4,7,10,13,16,19,22,25-nonathiacycloheptacosa-2,5,11,14,20,23-hexaene (11): mp 148.5-149.0 °C (from cyclohexane/CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 3.17 (8H, s, CH_2), 7.08-7.10 (4H, m), 7.15-7.23 (8H, m), 7.49-7.52 (4H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 33.8 (CH_2), 127.6 128.3, 131.7, 134.0, 135.1, 139.2; MS *m/z* 552 (M^+), 248, 216 (100%), 184. Anal. Calcd for $C_{28}H_{24}S_6$: C, 60.83; H, 4.38. Found: C, 60.81; H, 4.40.

Condensation of the Dithiol (4) with 1,3-Dibromopropane

The condensation was carried out in DMF under a variety of concentrations of the reactants. The followings gave the best results. To a stirred suspension of 360 mg (1.1 mmol) of Cs_2CO_3 in 70 ml of DMF were added simultaneously solutions of 250 mg (1.0 mmol) of **4** in 10 ml of DMF and 202 mg (1.0 mmol) of 1,2-dibromopropane in 10 ml of DMF over a period of 1 h at room temperature. The mixture was stirred for 24 h. The resulting mixture was purified as described above to give 123 mg (42%) of ***2H*-3,4-dihydrodibenzo[*f,i*][1,5,8]trithiecin (12)**: mp 72.5-73.0 °C (from hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 1.98 (2H, quintet, J = 6.2 Hz, $-CH_2C\underline{H}_2CH_2-$), 3.50 (4H, t, J = 6.2 Hz, $-C\underline{H}_2CH_2C\underline{H}_2-$), 7.18-7.24 (4H, m), 7.47-7.52 (2H, m), 7.56-7.61 (2H, m); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.7, 35.4, 128.6, 128.7, 134.5, 137.0, 139.6, 141.2; MS *m/z* 290 (M^+), 243, 216 (100%), 184. Anal. Calcd for $C_{15}H_{14}S_3$: C, 62.02; H, 4.86. Found: C, 62.19; H, 4.85.

Condensation of the Dithiol (4) with *cis*-1,2-Dichloroethylene

The followings gave the best results. A solution of sodium ethoxide was prepared by dissolving 60 mg (2.6 mmol) in ethanol (100 ml). To this solution were added 249 mg (1 mmol) of **4** and 97 mg (1 mmol) of *cis*-1,2-dichloroethylene. The mixture was heated under reflux for 6 h under argon and cooled to room temperature. The resulting white powder was collected by filtration and crystallized from chlorobenzene to give 55 mg (20%) of **16**. The filtrate of the original reaction mixture was evaporated and the residue was chromatographed on a column of alumina with hexane/CH_2Cl_2 (5:1) as the eluent to give 13 mg (5%) of **15** and 68 mg (25%) of **14** in this order.

Dibenzo[*b,e*][1,4,7]trithionin (14): mp 108.5-109.5 °C (from ethanol); ^1H NMR (300 MHz, $CDCl_3$) δ 6.48 (2H, s, alkenic H), 7.20-7.27 (4H, m, aromatic H), 7.41-7.47 (4H, m, aromatic H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 124.0, 128.7, 129.3, 134.35, 134.40, 135.0, 140.0; MS *m/z* 274 (M^+), 216 (100%), 184. Anal. Calcd for $C_{14}H_{10}S_3$: C, 61.27; H, 3.67. Found: C, 61.45; H, 3.65.

***2H*-2-Methylenedibenzo[*d,g*][1,3,6]trithiocin (15)**: mp 107-108 °C (from hexane); ^1H NMR (400 MHz, DMSO-d_6) δ 5.99 (2H, s, methylene H), 7.33-7.40 (4H, m, aromatic H), 7.51-7.53 (2H, m, aromatic H), 7.64-7.66 (2H, m, aromatic H); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 126.7, 129.0, 129.1, 131.6, 132.2, 136.6, 138.7, 140.3; MS *m/z* 274 (M^+), 216, 184, 133 (100%). Anal. Calcd for $C_{14}H_{10}S_3$: C, 61.27; H, 3.67. Found: C, 61.34; H, 3.81.

2,3:5,6:11,12:14,15-Tetrabenzo-1,4,7,10,13,16-hexathiacyclooctadeca-2,5,8,11,14,17-hexaene (16): mp 248-250 °C (from chlorobenzene); ^1H NMR (400 MHz, DMSO-d_6, at 337 K) δ 6.92 (4H, s, alkenic H), 7.17-7.21 (4H, m, aromatic H), 7.30-7.35 (4H, m, aromatic H), 7.36-7.41 (8H, m, aromatic H); MS *m/z* 548 (M^+). Anal. Calcd for $C_{28}H_{20}S_6$: C, 61.27; H, 3.67. Found: C, 61.56; H, 3.61.

X-Ray Crystallographic Analyses of 10, 14, and 15. Single crystals of **10**, **14**, and **15** were mounted on a MAC Science DIP3000 diffractometer with a graphite-monochrometer at 23 °C. Oscillation and nonscreen Weissenberg photographs were collected on the imaging plates of the diffractometer by using Mo-K_α radiation (λ = 0.71073 Å) and the data collection was made by the MAC XDIP program system. Cell parameters were determined and refined by using the MAC DENZO for all observed reflections. The structures were solved by direct methods using SIR[9] in the CRYSTAN-GM program system. The atomic coordinates and the anisotropic thermal parameters of the non-H atoms were refined by full matrix least squares.[10]

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