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Synthesis of Dibenzo[*d*,*g*][1,3,6]trithiocins

Teruo Maruta, Yoshiaki Sugihara, Sanae Tanaka, Akihiko Ishii, and Juzo Nakayama*

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338-8570

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6-Acetoxy-, 6-methoxy-, 6-azido-, and 6-(methylthio)dibenzo[*d*,*g*][1,3,6]trithiocins (**13**, **14**, **17**, and **18**, respectively) were synthesized by reactions of 9a*H*-9,10-dithia-4b-thioniaindeno[1,2-*a*]indene chloride (**4**) with appropriate nucleophiles in good yields. The trithiocin **13** was also prepared by the Pummerer reaction of dibenzo[*d*,*g*][1,3,6]trithiocin 5-oxide (**12**) in 97% yield. In many reactions of **4** with nucleophiles, the trimeric partial hydrolysis product, bis{*o*-[(dibenzo[*d*,*g*]-[1,3,6]trithiocin-6-yl)thio]phenyl} sulfide (**15**), was formed either as the major or a minor product. Structure of **15** was determined by X-ray diffraction analysis. Meanwhile, heating **4** in boiling methanol or ethanol gave the hydrolysis product, bis(*o*-mercaptophenyl) sulfide (**16**), in good yields. Condensation of **16** with benzaldehyde and pivalaldehyde gave 6-phenyl- and 6-*t*-butyldibenzo[*d*,*g*][1,3,6]trithiocins in good yields.

We have recently reported a convenient one-pot synthesis of a polycyclic sulfonium salt, 9a*H*-9,10-dithia-4b-thioniaindeno[1,2-*a*]indene chloride (**4**), by reaction of ethylene trithiocarbonate (**1**) with benzyne, generated by thermolysis of two molar amounts of 2-carboxybenzenediazonium chloride (**2**).[1,2] The reaction is initiated by 1,3-dipolar cycloaddition of benzyne to **1** to give a sulfonium ylide (**5**), which produces 1,3-benzodithiole-2-thione (**3**) and ethylene by a retro-1,3-dipolar cycloaddition. The dithiole-2-thione **3** further reacts with benzyne to give another ylide (**6**), which is more long-lived than **5**, and hence is trapped by hydrogen chloride, generated from **2**, to give **4** as the final product. Reduction of **4** with $NaBH_4$ gave dibenzo[*d*,*g*]-[1,3,6]trithiocin (**7**) in a high yield, while treatment with KOH in a mixture of ethanol and water gave the sulfoxide (**8**). Treatment of **4** with *t*-BuOK gave 6,6′-bidibenzo[*d*,*g*]-[1,3,6]trithiocinylidene (**9**) in a good yield; this is a higher analog of tetrathiafulvalene (Scheme 1).[2] Thus, the sulfonium salt **4** would serve as a convenient precursor of a range of dibenzo[*d*,*g*][1,3,6]trithiocins which had been a missing ring until our first report appeared. In addition, conformation analyses of **10**[3] and its heterocyclic analogs **11**[4,5] have been attracting increasing interest. Keeping this in mind, we have synthesized a series of dibenzo[*d*,*g*][1,3,6]trithiocins by reactions of **4** with nucleophiles.[6]

Results and Discussion

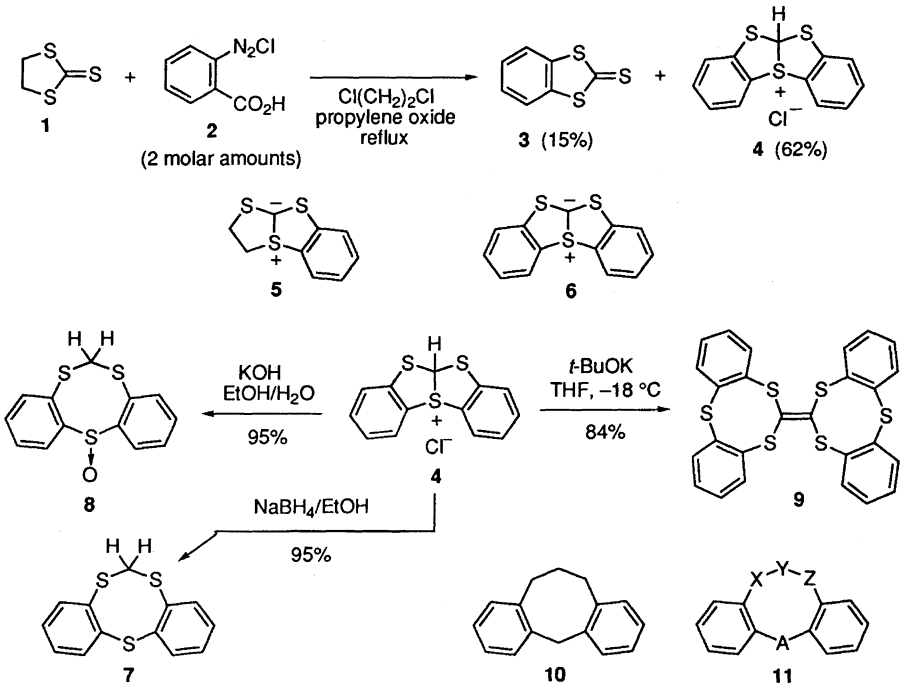
At the beginning of this study, we thought that many 6-substituted dibenzo[*d*,*g*][1,3,6]trithiocins would be obtainable by a simple S_N2 type reaction of the sulfonium salt **4** with nucleophiles, where heterolytic dissociation of the central C_1–S_6 bond is involved in the transition state. However, the reaction was much more complex than we had expected. Although, in some cases, the expected products were obtained in reasonable yields, many reactions did not take place in a clean manner and gave complex mixtures, as described below.

6-Acetoxydibenzo[*d*,*g*][1,3,6]trithiocin (**13**) was prepared in two ways. Oxidation of **7** with *m*-chloroperbenzoic acid (*m*-CPBA) gave an isomeric mixture of the sulfoxides **8** and **12** in 5 and 77% yields, respectively, with 11% recovery of **7** (Scheme 2). The Pummerer rearrangement of **12** in refluxing acetic anhydride gave the expected **13** in 97% yield. More conveniently, the trithiocin **13** was obtained in 80% yield by treatment of the sulfonium salt **4** with sodium acetate in acetonitrile. Treatment of **4** with sodium acetate in acetic acid also gave **13** in a decreased yield (33%).

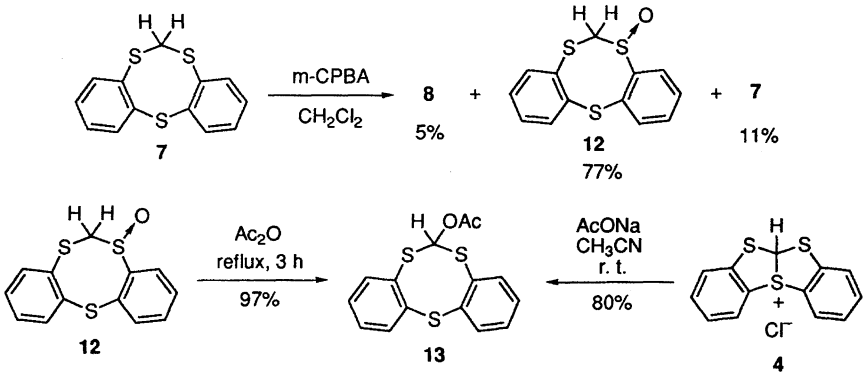
Treatment of **4** with methanol in the presence of sodium carbonate gave 6-methoxydibenzo[*d*,*g*][1,3,6]trithiocin (**14**) and the trimeric partial hydrolysis product (**15**) in 66 and 22% yields, respectively (Scheme 3). The use of sodium hydrogencarbonate instead of sodium carbonate gave **14** and **15** in 35 and 38% yields, respectively. Treatment of **4** with methanol in the presence of sodium methoxide also gave **14** and **15**, both in 30% yields. The formation of the trimeric product **15**, either as a major or minor product, was also found in some other reactions described below. The structure of **15** was determined by spectroscopic data and X-ray diffraction analysis (Fig. 1). Investigation on thiocrown ether-like properties of **15** in solution is under way; it provides an open table for soft guests between two trithiocin units.

When **4** was heated in refluxing methanol, an unexpected reaction took place to give the hydrolysis product **16** in 73% yield together with **14** and **15** in small amounts. The reaction provides a convenient synthesis of **16**, which is otherwise difficult to prepare.[7] Condensation of **16** with proper substrates would provide a promising route to a wide variety of dibenzo-annelated seven-membered-ring heterocyclic compounds. Heating **4** in refluxing ethanol also gave **16** in 69% yield.

Hydrolysis of **4** in a mixture of water and acetonitrile or in water alone gave complex mixtures containing **15**.



Scheme 1.



Scheme 2.

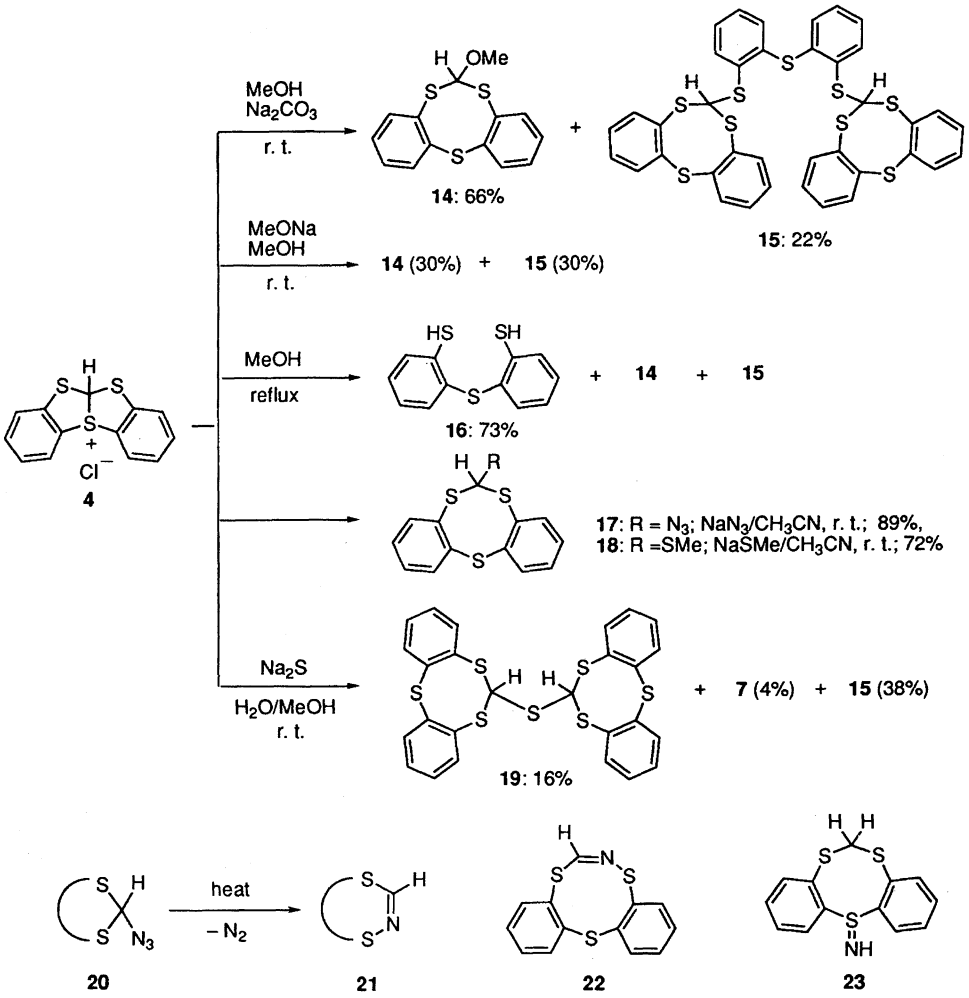
Thermally labile, crystalline 6-azidodibenzo[*d*,*g*][1,3,6]-trithiocin (**17**) was obtained in 89% yield by treatment of **4** with sodium azide in acetonitrile. It is well documented that thermolysis of azides like **20** often leads to ring-expansion products **21** in good yields, probably through insertion of nitrene intermediates into one of the C–S bond.[8] However, the thermolysis of **17** in refluxing benzene gave polymeric products which are insoluble in common organic solvents. No expected product **22** was formed. The thermolysis carried out in the presence of morpholine also gave similar results.

6-Methylthiodibenzo[*d*,*g*][1,3,6]trithiocin (**18**) was prepared in 72% yield by reaction of **4** with sodium methanethiolate in acetonitrile. The reaction of **4** with sodium sulfide in a mixture of methanol and water gave the sulfide **19**, though in a low yield (16%). In this case, the trimeric product **15** and the reduction product **7** were also formed in 38 and 4% yields.

The reaction of **4** with other nitrogen nucleophiles did not give any nitrogen-incorporated products. The reaction of **4** with ammonia was expected to give a sulfilimine **23** on the analogy of formation of the sulfoxide **8** by alkaline hydrolysis of **4**.[2] However, heating **4** with aqueous ammonia in acetonitrile gave the trimeric product **15** in 50% yield as the sole identifiable product. Even treatment of **4** with benzylamine or diethylamine in refluxing acetonitrile gave **15** in high yields as the sole product.

Reactions of **4** with MeMgI and BuLi in ether or THF did not give the expected alkyl-substituted trithiocin derivatives; the only identifiable products were the reduction product **7** and the dimeric product **9** in small amounts. Reactions of PhC≡CLi in THF and of KCN in a variety of solvents did not proceed in a clean manner. Ph_3P in acetonitrile and $P(OMe)_3$ in benzene are also nucleophiles which failed to react with **4** in a clean manner. In these cases, the trimeric product **15** was the only identifiable product.

Although 6-alkyldibenzo[*d*,*g*][1,3,6]trithiocins were not obtainable by reactions of **4** with MeMgI or BuLi, they could be easily synthesized from the thiol **16**. Thus, benzalde-



Scheme 3.

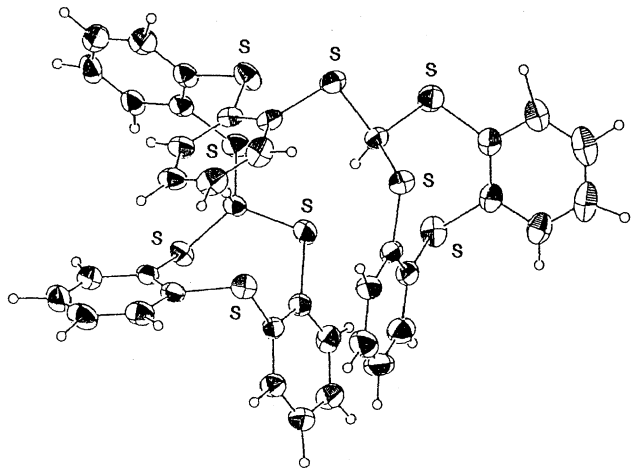
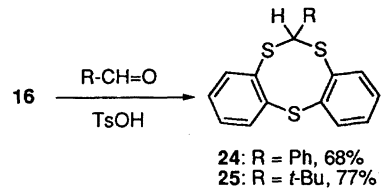


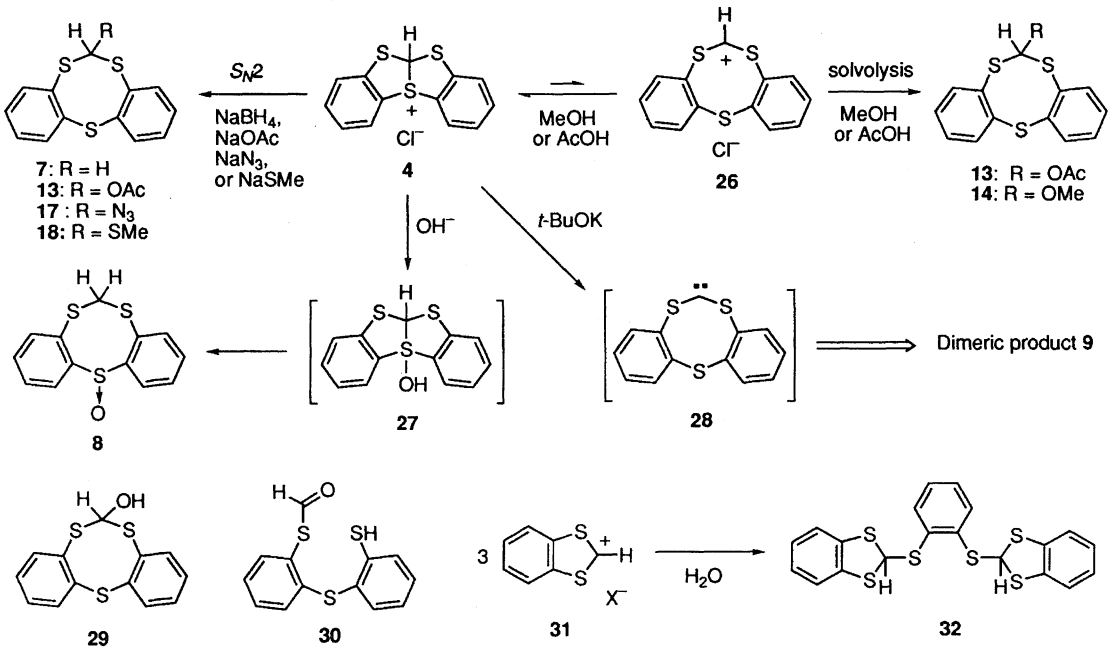
Fig. 1. An ORTEP drawing of **15** (ellipsoids at 30% probability).



Scheme 4.

hyde and pivalaldehyde condensed with **16** in the presence of *p*-toluenesulfonic acid to give **24** and **25** in 68 and 77% yields, respectively (Scheme 4).

The foregoing reactivities of **4** can be summarized as below. Reactions of **4** with nucleophiles such as $NaBH_4$, sodium acetate, sodium azide, and sodium methanethiolate in THF or acetonitrile, which afforded trithiocins **7**, **13**, **17**, and **18**, respectively, probably proceed in a usual S_N2 pathway, where the sulfonium sulfur atom serves as the leaving group. In the alkaline hydrolysis, addition of OH^- to the sulfonium sulfur atom, which yields a sulfurane **27**, takes place faster than the S_N2 reaction on the carbenium carbon atom (Scheme 5). The C–S bond cleavage of **27** followed by proton transfer would lead to the final product **8**. Nucleophiles, such as hydride, acetate, methanethiolate, and azide, also may add to the sulfonium sulfur atom, but the addition should be reversible, because the resulting sulfurane intermediates do not have any decomposition pathway to give stable products. Thus, the S_N2 pathway will dominate for reactions with these nucleophiles. In the case of the strong and bulky base, *t*-BuOK, the dimeric product **9** would be formed by a process involving the carbene intermediate **28** produced by proton abstraction. The formation of trithiocins



Scheme 5.

13 and **14** in acetic acid and methanol, respectively, would be explained as the result of the addition of acetic acid and methanol to the carbenium ion **26**. In these protic solvents, the sulfonium salt **4** may dissociate into the carbenium ion **26** by the C–S bond cleavage, though the concentration of **26** is not high enough to be detected by ^{1}H NMR.[2] The additives, such as Na_2CO_3, $NaHCO_3$, and NaOAc, will serve as the hydrogen chloride scavenger. Hydrolysis of **4** probably proceeds by addition of water to **26**. The resulting alcohol **29** is further hydrolyzed via **30** to give the arenethiol **16**. The rapid reaction of **16** with two molecules of **4** would produce the partial hydrolysis product **15**. This type of hydrolysis is precedented. Thus, 1,3-benzodithiolylium ion **31** is highly susceptible to hydrolysis under neutral to basic conditions, and is easily converted to the trimeric product **32** in high yield by contaminating water.[9] However, the predominant formation of **16** in refluxing methanol or ethanol still remains as an open question.

Experimental

General. 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 and a Bruker ARX400 spectrometers using $CDCl_3$ as the solvent with TMS as the internal standard (400 MHz for ^{1}H and 100.6 MHz for ^{13}C, respectively) at 25 °C, unless otherwise stated. IR spectra were taken on a Hitachi 270-50 spectrometer. Mass spectra were determined on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. The sulfonium salt **4** was prepared by the method developed by us.[1,2] Silica-gel column chromatography was performed on Keisel-gel Art 7734 (Merck, 70—230 mesh).

Oxidation of Dibenzo[*d*,*g*][1,3,6]trithiocin (7). A mixture of 392 mg (1.49 mmol) of **7** and 285 mg (1.65 mmol) of *m*-CPBA in 10 ml of CH_2Cl_2 was stirred for 3 h at room temperature. The mixture was washed with aqueous $NaHCO_3$ and water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on a column of silica gel. The column was eluted with a mixture of CH_2Cl_2 and AcOEt (5 : 1) to give 41 mg (11%) of **7**, 22 mg (5%) of dibenzo[*d*,*g*][1,3,6]trithiocin 12-oxide (**8**), mp 219.5—221.0 °C (lit,[2] mp 221—222 °C), and 318 mg (77%) of dibenzo[*d*,*g*][1,3,6]trithiocin 5-oxide (**12**) in this order. **12**: Colorless needles (from AcOEt); mp 176—177 °C; ^{1}H NMR (55 °C) δ = 4.06 (1H, d, J = 14.2 Hz), 4.83 (1H, br s), 7.19 (1H, br t, J = 7.5 Hz), 7.27 (1H, dt, J = 7.5/1.3 Hz), 7.42—7.48 (2H, m), 7.54—7.64 (2H, m) 7.74 (1H, br d), 7.86 (1H, dd, J = 7.5/1.3 Hz); ^{13}C NMR (55 °C) δ = 64.66, 125.65, 128.78, 129.18, 130.40, 131.69, 134.17, 135.15, 136.28, 137.89, 150.84; IR (KBr) 1058 cm^{-1} (SO); MS(EI) *m*/*z* 278 (M^+), 230 $(M-SO)^+$, 153 (1,3-benzodithiolylium ion, 100%). Found: C, 56.37; H, 3.58%. Calcd for $C_{13}H_{10}OS_3$: C, 56.08; H, 3.62%.

6-Acetoxydibenzo[*d*,*g*][1,3,6]trithiocin (13) by Pummerer Reaction of the Sulfoxide 12. The sulfoxide **12** (425 mg, 1.53 mmol) was heated in boiling acetic anhydride (40 ml) for 3 h. The mixture was evaporated under reduced pressure, and the residue was chromatographed on a column of silica gel. The column was eluted with an 1 : 1 mixture of hexane and CH_2Cl_2 to give 370 mg (97%) of **13**: Colorless plates (from hexane); mp 114.5—115.0 °C; ^{1}H NMR δ = 2.12 (3H, s), 7.22 (2H, dt, J = 7.5/1.5 Hz), 7.30 (2H, dt, J = 7.5/1.5 Hz), 7.41 (1H, br s), 7.48 (2H, br d, J = 7.5 Hz), 7.62 (2H, br d, J = 7.5 Hz); ^{13}C NMR δ = 20.88, 85.94, 127.88, 129.84, 132.71, 135.05, 136.82, 139.56, 168.34; MS (EI) *m*/*z* 320 (M^+), 292, 250 (100%), 217, 184, 140. Found: C, 56.27; H, 3.75%. Calcd for $C_{15}H_{12}O_2S_3$: C, 56.22; H, 3.77%.

6-Acetoxydibenzo[*d*,*g*][1,3,6]trithiocin (13) from the Sulfonium Salt 4. A mixture of the sulfonium salt **4** (2.00 g, 6.75 mmol) and sodium acetate (1.86 g, 13.7 mmol) in acetonitrile (200 ml) was stirred for 24 h at room temperature. The insoluble material was removed by filtration and the filtrate was evaporated. The residue was recrystallized from hexane to give 1.73 g (80%) of **13**. Stirring a mixture of **4** (205 mg, 0.69 mmol) and sodium acetate (188 mg, 1.38 mmol) in acetic acid (20 ml) for 27 h at room temperature gave 72 mg (33%) of **13**.

6-Methoxydibenzo[*d*,*g*][1,3,6]trithiocin (14) and Bis{*o*-[(dibenzo[*d*,*g*][1,3,6]trithiocin-6-yl)thio]phenyl} Sulfide (15) from Sulfonium Salt 4. A mixture of the sulfonium salt **4** (594 mg, 2 mmol) and sodium carbonate (423 mg, 4 mmol) in methanol (30 ml) was stirred for 22 h at room temperature. The mixture was poured onto a mixture of iced-water and ether (50 ml). The crystalline insoluble material was collected by filtration to give 115 mg (22%) of **15**. The ether layer of the filtrate was dried over $MgSO_4$ and evaporated to give 387 mg (66%) of nearly pure **14** as a viscous oil, which solidified slowly on standing. The pure **14** was obtained by recrystallization from hexane: Colorless crystals; mp 64.0—64.5 °C; ^{1}H NMR δ = 3.57 (3H, s), 6.63 (1H, br s), 7.20 (2H, dt, J = 7.5/1.3 Hz), 7.27 (2H, dt, J = 7.5/1.3 Hz), 7.48 (2H, br d, J = 7.5 Hz), 7.61 (2H, br d, J = 7.5 Hz); ^{13}C NMR δ = 57.60, 98.43, 127.95, 129.23, 133.88, 135.56, 137.63, 137.87; IR (KBr) 3050, 3001, 2943, 2916, 2905, 2812, 1446, 1418, 1186, 1163, 1066, 1042 cm^{-1}; MS (EI) *m/z* 292 (M^+), 216 (100%), 183. Found: C, 57.55; H, 4.09%. Calcd for $C_{14}H_{12}OS_3$: C, 57.50; H, 4.14%. **15**: Colorless plates (from CH_2Cl_2/hexane); mp 182—182.5 °C; ^{1}H NMR δ = 6.56 (2H, s), 7.00 (2H, br d, J = 7.5 Hz), 7.13 (2H, br t, J = 7.5 Hz), 7.17—7.22 (6H, m), 7.26 (4H, br t, J = 7.5 Hz), 7.43 (4H, dd, J = 7.5/1.4 Hz), 7.54—7.62 (6H, m); ^{13}C NMR δ = 62.40, 127.66, 128.21, 128.77, 129.23, 131.78, 133.12, 134.59, 134.90, 135.78, 136.18, 137.74, 139.43. Found: C, 59.08; H, 3.33%. Calcd for $C_{38}H_{26}S_9$: C, 59.18; H, 3.40%.

Stirring a mixture of **4** (297 mg, 1 mmol) and sodium hydrogencarbonate (168 mg, 2 mmol) in methanol (15 ml) for 3 d at room temperature gave 101 mg (35%) of **14** and 97 mg (38%) of **15**.

Stirring a mixture of **4** (207 mg, 0.7 mmol) and sodium methoxide (78 mg, 1.4 mmol) in methanol (6 ml) for 3 d at room temperature gave 61 mg (30%) of **14** and 54 mg (30%) of **15**.

Bis(*o*-mercaptophenyl) Sulfide (16) from Sulfonium Salt 4. The sulfonium salt **4** (593 mg, 2 mmol) was heated in refluxing methanol (20 ml) for 2 h. The mixture was evaporated and the residue was partitioned between 2 M NaOH (50 ml) (1 M = 1 mol dm^{-3}) and CH_2Cl_2 (100 ml). The alkaline layer was acidified by concentrated hydrochloric acid and extracted with CH_2Cl_2. The extracts were washed with water, dried over $MgSO_4$, and evaporated to give 365 mg (73%) of **16**: mp 91—92 °C (lit,[6] mp 90—91 °C); ^{1}H NMR δ = 4.07 (2H, s, SH), 7.05—7.18 (6H, m), 7.37—7.39 (2H, m); ^{13}C NMR δ = 126.49, 128.21, 130.09, 132.26, 132.32, 134.89. Evaporation of the original CH_2Cl_2 layer, after it had been washed with water and dried over $MgSO_4$, gave a mixture of the dithiocin **14** and the trimeric product **15**.

6-Azidodibenzo[*d*,*g*][1,3,6]trithiocin (17). A mixture of the sulfonium salt **4** (2.01 g, 6.76 mmol) and sodium azide (0.89 g, 13.7 mmol) in acetonitrile (200 ml) was stirred for 3 h at room temperature. The mixture was diluted with iced-water, extracted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and evaporated to give 1.83 g (89%) of crude **17**; pale yellow crystals (from hexane), mp 54.0—56.5 °C; ^{1}H NMR δ = 6.42 (1H, br s), 7.25 (2H, dt, J = 7.4/1.3 Hz), 7.33 (2H, dt, J = 7.4/1.3 Hz), 7.52 (2H, br d, J = 7.4 Hz), 7.64 (2H, br d, J = 7.4 Hz); ^{13}C NMR δ = 76.12, 128.29, 129.77, 134.35 (overlapping of two signals), 135.46, 137.17; IR (KBr) 3054, 2958, 2926, 2114 (N_3), 1571, 1447, 1427, 1210 cm^{-1}; MS (FAB) *m/z* 303 (M^+), 261, 248, 216 (100%). Found: C, 51.63; H, 2.93; N, 13.55%. Calcd for $C_{13}H_9N_3S_3$: C, 51.46; H, 2.99; N, 13.85%.

6-Methylthiodibenzo[*d*,*g*][1,3,6]trithiocin (18) from Sulfonium Salt 4. A mixture of 203 mg (0.68 mmol) and 98 mg (1.4 mmol) of sodium methanethiolate in acetonitrile (20 ml) was stirred for 24 h at room temperature. The insoluble material (NaCl) was removed by filtration and the filtrate was evaporated. The residue was chromatographed on a column of silica gel with a 1 : 2 mixture of CH_2Cl_2 and hexane as the eluent to give 152 mg (72%) of **18**: Colorless crystals (from cyclohexane); mp 84.5—85.0 °C; ^{1}H NMR δ = 2.41 (3H, s), 6.31 (1H, br s), 7.22 (2H, dt, J = 7.4/1.3 Hz), 7.28 (2H, dt, J = 7.4/1.3 Hz), 7.46 (2H, br d, J = 7.4 Hz), 7.62 (2H, br d, J = 7.4 Hz); ^{13}C NMR δ = 15.58, 62.04, 128.32, 129.08, 133.67, 134.95, 135.69, 140.42; MS (EI) *m/z* 308 (M^+), 216 (100%), 199, 184, 153. Found: C, 54.76; H, 3.86%. Calcd for $C_{14}H_{12}S_4$: C, 54.51; H, 3.92%.

Bis[dibenzo[*d*,*g*][1,3,6]trithiocin-6-yl] Sulfide (19) from Sulfonium Salt 4. To an ice-cooled solution of **4** (594 mg, 2 mmol) in methanol (15 ml) was added dropwise a 1 M aqueous solution of sodium sulfide nonahydrate (1 ml, 1 mmol) and the mixture was stirred for 4 h at room temperature. The insoluble material which separated was collected by filtration, air-dried, and chromatographed on a column of silica gel. The column was eluted with a 1 : 2 mixture of CH_2Cl_2 and hexane to give 10 mg (4%) of the trithiocin **7**, 87 mg (16%) of the sulfide **19**, and 194 mg (38%) of the trimeric product **15** in this order. **19**: Colorless needles (CCl_4/hexane); mp 174.8—175.4 °C; ^{1}H NMR δ = 6.53 (2H, s), 7.11 (4H, br t, J = 7.5 Hz), 7.24 (4H, m), 7.29 (4H, br d, J = 7.5 Hz), 7.56 (4H, br d, J = 7.5 Hz); ^{13}C NMR δ = 62.60, 128.35, 129.35, 134.42, 134.91, 135.95, 139.01; MS (EI) *m/z* 554 (M^+), 261 (100%). Found: C, 56.04; H, 3.19%. Calcd for $C_{26}H_{18}S_7$: C, 56.28; H, 3.27%.

Reactions of 4 with Nitrogen Nucleophiles. A mixture of 207 mg (0.70 mmol) of **4** and 210 mg of 29% aqueous ammonia (3.6 mmol) in acetonitrile (20 ml) was heated under reflux for 1 h. Purification of the mixture by silica-gel column chromatography gave 89 mg (50%) of **15**. Similarly, stirring a mixture of **4** (203 mg, 0.68 mmol) and benzylamine (365 mg, 3.4 mmol) in aceonitrile (20 ml) for 24 h at room temperature gave 158 mg (90%) of **15**. Stirring a mixture of 292 mg (1 mmol) of **4** and diethylamine (731 mg, 10 mmol) in acetonitrile (20 ml) for 48 h at room temperature gave 234 mg (91%) of **15**.

6-Phenyl- and 6-*t*-Butyldibenzo[*d*,*g*][1,3,6]trithiocins (24) and (25). A mixture of the arenethiol **16** (101 mg, 0.4 mmol), and benzaldehyde (52 mg, 0.5 mmol), and *p*-toluenesulfonic acid monohydrate (20 mg) in 40 ml of toluene was heated at reflux for 23 h. The resulting mixture was purified by silica-gel column chromatography to give 93 mg (68%) of **24**. The trithiocin **25** was also prepared in 77% yield by heating a mixture at reflux for 40 h. **24**: Colorless needles (from hexane); mp 110.0—110.5 °C; ^{1}H NMR δ = 6.42 (1H, s), 7.18—7.40 (11H, m), 7.67 (2H, br d, J = 7.0 Hz); ^{13}C NMR δ = 60.21, 127.97, 128.04, 128.26, 128.61, 128.84, 134.34, 135.26, 135.66, 139.84, 140.25; MS (EI) *m/z* 338 (M^+), 229 (100%), 216, 184. Found: C, 67.28; H, 4.11%. Calcd for $C_{19}H_{14}S_3$: C, 67.41; H, 4.17%. **25**: Colorless plates (from MeOH); mp 122.0—122.5 °C; ^{1}H NMR δ = 1.14 (9H, s), 5.38 (1H, s), 7.09 (2H, dt, J = 7.5/1.2 Hz), 7.15 (2H, dt, J = 7.5/1.2 Hz), 7.34 (2H, dd, J = 7.5/1.2 Hz), 7.53 (2H, dd, J = 7.5/1.2 Hz); ^{13}C NMR δ = 27.68, 38.10, 70.04, 128.14, 128.33, 133.28, 134.45, 136.26, 142.37. Found: C, 64.16; H, 5.66%. Calcd for $C_{17}H_{18}S_3$: C, 64.10; H, 5.70%.

X-Ray Diffraction Analysis of 15. Crystal data for **15**: $C_{38}H_{26}S_9$, monoclinic, *C*2/*c* (No. 15), a = 18.229(3), b = 10.2140(8), c = 39.041(4) Å, β = 99.901(7)°, V = 7161(1) Å^3, Z = 8, ρ_{calcd} = 1.453 g cm^{-3}, μ(Mo $K\alpha$) = 2.893 mm^{-1}. A colorless cube with dimensions 0.34×0.28×0.16 mm was mounted on a Mac Science DIP3000 diffractometer with a graphite-monochromator. Oscillation and nonscreen Weissenberg photographs were recorded on

the imaging plates of the diffractometer by using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 25 °C and the data reduction was made by the MAC DENZO program system. Intensity data of 9047 reflections (7578 independent reflections) were collected in the range of $0 \leq h \leq 25$, $0 \leq k \leq 13$, $-55 \leq l \leq 54$ (θ_{max} 28.95°). Cell parameters were determined and refined by using MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR[10] 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[11] to minimize the functions $\Sigma(|F_o| - |F_c|)^2$ for 4879 reflections [$I > 2\sigma(I)$] (425 parameters). The final R (R_w) = 0.051 (0.048) and GOF = 2.464; max/min residual electron density = 0.26/ − 0.33 eÅ^{-3}.

Tables of the fractional atomic coordinates and U_{iso}, the anisotropic thermal parameters, all bond lengths, angles, and torsion angles, and the complete $F_o - F_c$ data are deposited as Document No. 71026 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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