Synthesis, Structure, and Ring Conversion of 1,2-Dithiete and Related Compounds

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3,4-Bis(methoxycarbonyl)-1,2-dithiete (**6**), 3,4,7,8-tetrakis(methoxycarbonyl)-1,2,5,6-tetrathiocin (**8**), and (*Z,Z,Z,Z*)-3,4,7,8,11,12,15,16-octakis(methoxycarbonyl)-1,2,5,6,9,10,13,14-octathiacyclohexadeca-3,7,11,15-tetraene (**9**) were synthesized by oxidation of titanocene dithiolene complex **4** with sulfuryl chloride, and the crystal structures of **6** and **8** were characterized by X-ray crystallographic analysis which revealed planar and twist geometries, respectively. Tetrathiocin **1**, **11**, and **12**, and 16-membered cyclic compound **3** were also obtained by oxidation of the corresponding dithiolate or dithiolene complex. Dithiete **6** underwent tetramerization selectively to give 16-membered cyclic product **9** even at room temperature. Ring conversion reactions also proceeded among the 4-, 8-, and 16-membered unsaturated cyclic compounds possessing disulfide bonds under various conditions, such as in polar solvent or in the presence of silica gel. The ring-size selectivity of these ring conversion reactions was studied using ab initio molecular orbital calculations.

Introduction

The unsaturated cyclic compound cyclooct-1,5-diene has been the subject of considerable interest, especially its conformational behavior[1,2] and as a ligand of organometallic complexes. Cyclooct-1,5-diene derivatives substituted with heteroatoms in place of sp³-hybridized carbons are also of great interest in view of their conformation and reactivity. However, only a few compounds consisting of a monocyclic system with a disulfide[3,4] or diselenide[5] bond are known. Recently, we succeeded in synthesizing 1,2,5,6-tetrathiocin (1,2,5,6-tetrathiacyclooct-3,7-diene) with the most fundamental substituents, hydrogen atoms, and examined its photochemical behavior.[6] On the other hand, the smallest unsaturated cyclic system with a disulfide bond, 1,2-dithiete, has also been the focus of interest because of its structure, unique bonding properties, and relation to its valence isomer, ethane-1,2-dithione.[7] After an isolable

1,2-dithiete, 3,4-bis(trifluoromethyl)-1,2-dithiete, was obtained for the first time by Krespan and co-workers in 1960,[3a] several 1,2-dithietes have been isolated[8] or generated.[9] Krespan et al. also reported that 3,4-bis(trifluoromethyl)-1,2-dithiete underwent dimerization to give a 1,2,5,6-tetrathiocin derivative.[3] We succeeded in synthesizing 3,4-bis(methoxycarbonyl)-1,2-dithiete and related compounds by oxidation of the corresponding titanocene dithiolene complex. We also found that tetramerization of 3,4-bis(methoxycarbonyl)-1,2-dithiete took place selectively to give an unsaturated 16-membered cyclic compound possessing disulfide units under various

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Scheme 1

Z = CO$_2$Me
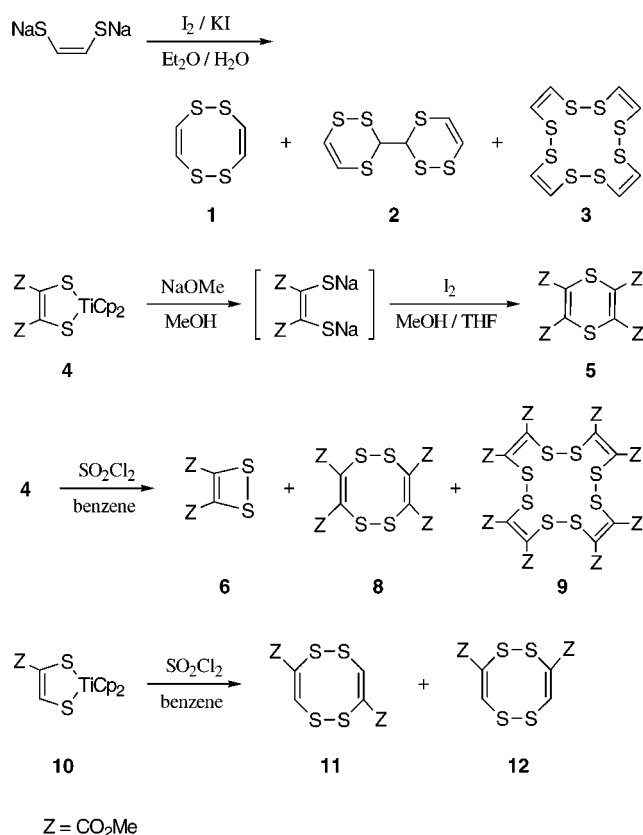
conditions. In this paper, we report the synthesis, structure, and novel ring conversion reactions of 1,2-dithiete and related compounds. The conformations and relative energies of molecules of this type are also discussed on the basis of ab initio molecular orbital calculations to study the ring-size selectivity of the ring conversion reaction.

Results and Discussion

Synthesis of 1,2-Dithiete and Related Compounds. Oxidation of disodium *cis*-ethene-1,2-dithiolate, prepared from *cis*-1,2-bis(benzylthio)ethene and sodium,[10] with iodine/potassium iodide at −10 °C in a heterogeneous solution under dilution conditions gave 1,2,5,6-tetrathiocin (**1**) in 14% yield together with small amounts of 3,3′-bi(3*H*-1,2,4-trithiinyl) (**2**) (*meso*/*dl* = 2/5) (0.5%) and (*Z,Z,Z,Z*)-1,2,5,6,9,10,13,14-octathiacyclohexadeca-3,7,-11,15-tetraene (**3**) (2.0%) (Scheme 1).[6] However, the monocyclic trimer 1,2,5,6,9,10-hexathiacyclododeca-3,7,-11-triene, expected to be formed in this reaction, was not obtained. Furthermore, the smallest cyclic compound, 1,2-dithiete, also expected to be formed as an unstable species, was not detected.

We also planned to prepare a substituted ethene-1,2-dithiolate derivative as a precursor of cyclic compounds by a similar method. However, preparation of a substituted ethene-1,2-dithiolate using this method is known to be difficult.[11] Therefore, we prepared a titanocene dithiolene complex **4**[12] with methoxycarbonyl groups as a synthon of the disodium ethene-1,2-dithiolate deriva-

tive, and oxidation of **4** was carried out under various conditions. Oxidation of **4** with iodine did not proceed in either tetrahydrofuran or ether, and oxidation with sulfuryl chloride in tetrahydrofuran or acetonitrile gave a complex mixture. Furthermore, iodine oxidation of the disodium dithiolate, prepared in situ by the reaction of **4** with sodium methoxide, in methanol/tetrahydrofuran solution formed 2,3,5,6-tetrakis(methoxycarbonyl)-1,4-dithiin (**5**) in 39% yield. The formation of 1,4-dithiin **5** might be due to cycloaddition between 1,2-dithiete **6** and ethane-1,2-dithione to give bicyclic compound **7**, followed
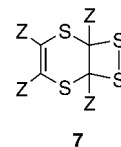
by the extrusion of two sulfur atoms.[9a,b,l] Finally, successful oxidation of complex **4** was achieved with sulfuryl chloride in benzene under dilution conditions to form 3,4-bis(methoxycarbonyl)-1,2-dithiete (**6**), which has been suggested to be generated as an intermediate by the reaction of dimethyl acetylenedicarboxylate with elemental sulfur by Nakayama et al.,[9m,n] in 66% yield together with small amounts of 3,4,7,8-tetrakis(methoxycarbonyl)-1,2,5,6-tetrathiocin (**8**) (1.6%), and (*Z,Z,Z,Z*)-3,4,7,8,11,-12,15,16-octakis(methoxycarbonyl)-1,2,5,6,9,10,13,14-octathiacyclohexadeca-3,7,11,15-tetraene (**9**) (2.0%).

On the other hand, oxidation of a titanocene dithiolene complex possessing one methoxycarbonyl group **10** with sulfuryl chloride gave tetrathiocin derivatives **11** and **12** in yields of 22 and 17%, respectively. However, the dithiete was not obtained.

Structure of 1,2-Dithiete and Tetrathiocin. The molecular structures of the products **1**,[6] *meso*-**2**,[13] and **3**[6] were determined by X-ray crystallographic analysis, and tetrathiocin **1** and tetramer **3** were found to show twist and cage structures, respectively, in their crystalline states.

We also determined the crystal structure of dithiete **6**, as shown in Figure 1. The length of the sulfur−sulfur bond in **6** is almost normal (2.07 Å), and that of the carbon−carbon double bond (1.36 Å) is slightly greater than the corresponding strain-free bonds in 8-membered cyclic compounds **1** (1.33 Å)[6] and **8** (1.34 Å, average). The bond angles around the 1,2-dithiete skeleton are, of course, highly strained; the angles around the sulfur atoms, C(4)−S(1)−S(2) and S(1)−S(2)−C(3), are 78.2 and 78.3°, and the angles S(2)−C(3)−C(4) and C(3)−C(4)−S(1) are 102.0 and 101.5°, respectively. The most interesting aspect of the structure of **6** is the planarity of the 4-membered ring. The dihedral angles around the dithiete ring are 0.1°, indicating a planar geometry. Furthermore, two methoxycarbonyl groups are almost coplanar with the ring. The crystal structures of benzo-dithiete[8a] and sterically hindered 1,2-dithiete[14] have been determined by Boar et al. and Nakayama et al., respectively, to also show a planar geometry for 1,2-dithiete moieties. However, those dithietes are fused or sterically controlled compounds. Therefore, the crystal structure of **6** is a good example of a natural geometry

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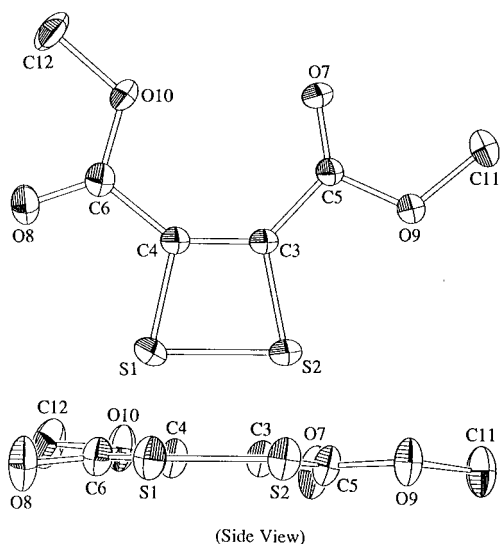
Figure 1. Crystal structure of **6** showing 30% probability displacement ellipsoids with hydrogen atoms removed for clarity. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): S(1)−S(2), 2.072(3); S(2)−C(3), 1.738-(7); C(3)−C(4), 1.36(1); C(4)−S(1), 1.746(7); C(3)−C(5), 1.463-(10); C(4)−C(6), 1.46(1); C(4)−S(1)−S(2), 78.2(3); S(1)−S(2)−C(3), 78.3(3); S(2)−C(3)−C(4), 102.0(5); C(3)−C(4)−S(1), 101.5(5); S(2)−C(3)−C(5), 124.8(6); S(1)−C(4)−C(6), 117.0(6); C(4)−C(3)−C(5), 132.9(7); C(3)−C(4)−C(6), 141.5(7); C(4)−S(1)−S(2)−C(3), 0.1(3); S(1)−S(2)−C(3)−C(4), −0.1(4); S(2)−C(3)−C(4)−S(1), 0.1(5); C(3)−C(4)−S(1)−S(2), −0.1(4).

without any conformational restrictions. The geometry of 3,4-bis(trifluoromethyl)-1,2-dithiete was also studied by Hencher et al. using electron diffraction.[15]

Krespan et al. noted that 3,4-bis(trifluoromethyl)-1,2-dithiete had an aromatic character,[3] while Bergson reported the same finding for 1,2-dithietes.[16] The crystal structure of dithiete **6** showed a planar geometry for the ring system, despite that the dihedral angle around the sulfur−sulfur bond, 0.1°, is strained (ca. 11.5 kcal mol⁻¹) compared to those calculated for disulfides with strain-free geometries (ca. 90°).[17,18] Furthermore, the length of the carbon−carbon double bond in **6** is slightly greater than corresponding bonds in 8-membered cyclic compounds **1** and **8**. The planarity seems to have some aromaticity with 6π system in the ring of **6**. However, whether the dithiete has aromaticity or not is uncertain because steadfast evidence has not yet been obtained. The ¹³C NMR chemical shift of the sp²-hybridized carbons of the dithiete ring **6** (132 ppm) is similar to those of dimer **8** (137 ppm) and tetramer **9** (140 ppm).

The crystal structure of 3,4,7,8-tetrakis(methoxycarbonyl)-1,2,5,6-tetrathiocin (**8**) was also determined by X-ray analysis (Figure 2). The crystal structure of **8** shows a twist geometry similar to that of 1,2,5,6-tetrathiocin (**1**)[6] and the calculated geometry[17] at the global minimum for **1**. This is in contrast to the twist-boat form, which is the optimal geometry for cycloocta-
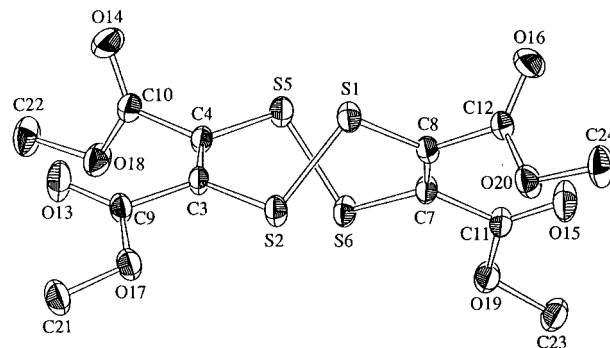

Figure 2. Crystal structure of **8** (*S*-conformer) showing 30% probability displacement ellipsoids with hydrogen atoms removed for clarity. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg): S(1)−S(2), 2.0533(5); S(2)−C(3), 1.762(2); C(3)−C(4), 1.340(2); C(4)−S(5), 1.755(1); S(5)−S(6), 2.0472(7); S(6)−C(7), 1.760(1); C(7)−C(8), 1.347(2); C(8)−S(1), 1.754(2); C(8)−S(1)−S(2), 103.26(5); S(1)−S(2)−C(3), 104.26-(5); S(2)−C(3)−C(4), 126.8(1); C(3)−C(4)−S(5), 128.2(1); C(4)−S(5)−S(6), 103.08(6); S(5)−S(6)−C(7), 104.30(7); S(6)−C(7)−C(8), 126.7(1); C(7)−C(8)−S(1), 128.1(1); C(8)−S(1)−S(2)−C(3), −111.64(8); S(1)−S(2)−C(3)−C(4), 40.5(2); S(2)−C(3)−C(4)−S(5), 6.8(3); C(3)−C(4)−S(5)−S(6), 44.9(2); C(4)−S(5)−S(6)−C(7), −112.03(7); S(5)−S(6)−C(7)−C(8), 40.6(1); S(6)−C(7)−C(8)−S(1), 7.0(2); C(7)−C(8)−S(1)−S(2), 44.6(2).

1,5-diene.[1g] In addition, the crystal consisted of a 1:1 racemic mixture. Some tetrathiocin derivatives with fused olefin moieties have been reported to show a chair conformation in their crystalline states.[19] This difference in conformations is believed to be due to the fused or non-fused structure of the olefin moieties. Therefore, the crystal structures of **1** and **8** reflect the natural geometry for 1,2,5,6-tetrathiocin. The bond lengths and angles of **8** are almost normal, and the dihedral angles around the olefin moieties are also strain-free (6.9°, average). The dihedral angles around the sulfur−sulfur bonds (C−S−S−C; 111.8°, average) are slightly extended compared with those in the most stable geometry for disulfides. An interesting feature of the crystal structure of **8** is the nonbonding interatomic distances between sulfur atoms. The distances S(1)−S(5), S(2)−S(6), S(1)−S(6), and S(2)−S(5) are 3.25, 3.32, 3.48, and 3.48 Å, respectively: these values are slightly shorter than twice the van der Waals radius of a sulfur atom (3.70 Å). The crystal structure of **11** also showed a geometry similar to that of **8**.

The UV spectra of tetrathiocin derivatives **1** and **8** show absorption maxima at 357 and 372 nm, respectively, whereas dithiete **6** and larger cyclic compounds **3** and **9** have absorption maxima at lower wavelengths, as shown in Figure 3. This difference between the UV spectra of tetrathiocins and other cyclic compounds might be caused by the interaction of a π-orbital on the carbon atoms of the olefin with lone pairs on adjoining sulfur atoms due to the conformation of the tetrathiocins.

Ring Conversion of 1,2-Dithiete and Related Compounds. A chloroform solution of 1,2-dithiete **6** formed octathiacyclohexadecatetraene **9** in 71% yield, together with a small amount of tetrathiocin **8** (4.8%),

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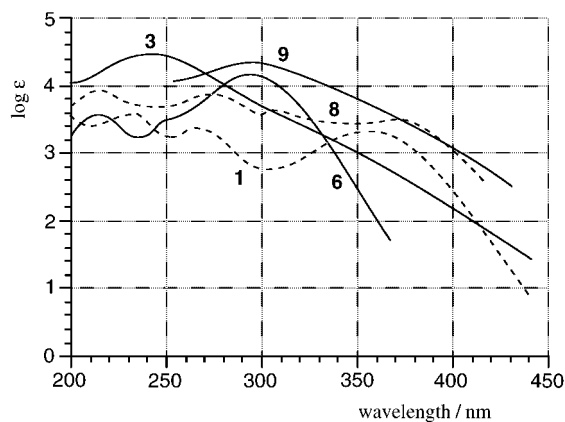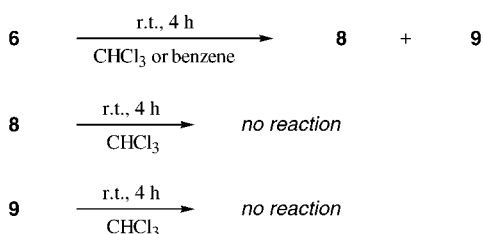
Figure 3. UV spectra of the cyclic compounds **1**, **3**, **6**, and **8** in cyclohexane and **9** in chloroform.

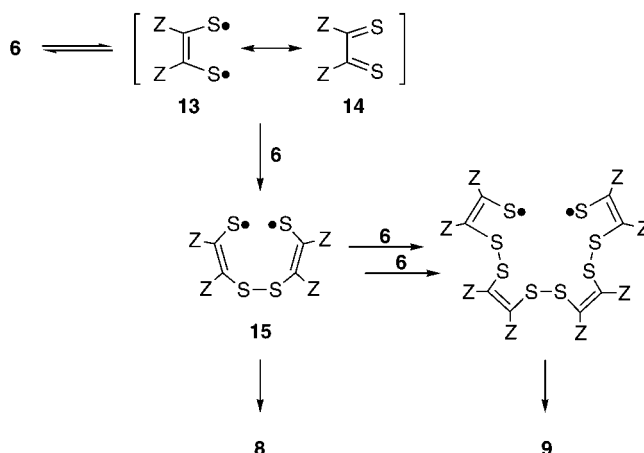**Scheme 2**

Scheme 3

Scheme 4

by standing at room temperature for 4 h (Scheme 2). The 16-membered cyclic compound **9** was also obtained from **6** in 74% yield in a benzene solution along with **8** in 6.1% yield. Although 3,4-bis(trifluoromethyl)-1,2-dithiete has been reported to dimerize to give a tetrathiocin derivative and an equilibrium exists among them,[3] the 1,2-dithiete **6** gave tetramer **9** in high selectivity. Furthermore, this reaction was irreversible, since tetrathiocin **8** and 16-membered cyclic compound **9** were stable in chloroform even after 4 h and the starting materials were recovered. When a mixture of the same amounts of **6** and **8** by weight was stirred in chloroform for 4 h, almost the same amount of **8** was recovered, and **6** and **9** were obtained in a weight ratio of 1:1.1. This result indicates that the 16-membered cyclic compound **9** is not a secondary product from **8**, and **8** does not react with **6** under the conditions. This reaction may be caused by the high reactivity of dithiete **6** due to the ring strains. As a result, this reaction is considered to proceed via biradical **13** or 1,2-dithione **14**, which is generated as the tautomer[8e−g,9h−o,20] of **6**, as shown in Scheme 3. Biradical **13** or 1,2-dithione **14** reacts with 1,2-dithiete **6** to give biradical **15**, and ring-closure of **15** gives tetrathiocin **8**. Subsequent twice addition of **15** to dithiete **6** followed by ring-closure gives 16-membered cyclic compound **9**.

A chloroform/acetonitrile solution (1:4) of 1,2-dithiete **6** also gave tetrathiocin **8** and tetramer **9** in yields of 19 and 41%, respectively (Scheme 4). The product ratio of tetrathiocin **8** was greater than that in the above-mentioned reaction in chloroform or benzene solution. Under this condition, tetrathiocin **8** also reacted to give 1,2-dithiete **6** and ring-expansion product **9** in yields of 13 and 44%, respectively. Tetrathiocin **8** was also transformed in a chloroform/ethanol solution (1:4) into **9** in 74% yield together with a trace amount of dithiete **6**. Although tetrakis(trifluoromethyl)-1,2,5,6-tetrathiocin
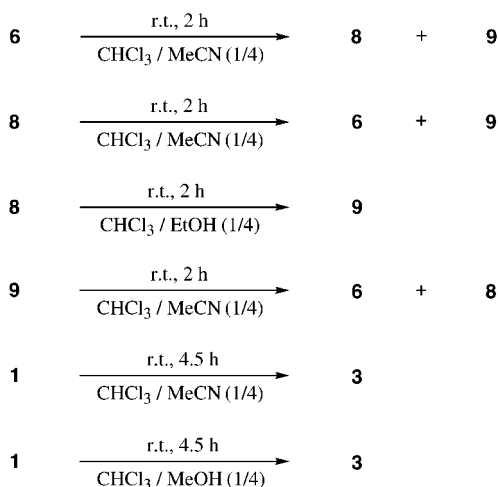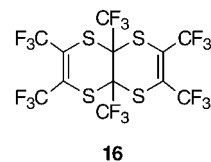
has been reported to react in ethanol solution to form dithiinodithiin **16**,[3] this type of compound was not

16

obtained in this reaction. Furthermore, 16-membered cyclic compound **9** also formed dithiete **6** and tetrathiocin **8** in yields of 5.8 and 12%, respectively, under the conditions. A long reaction time led to overreaction of the product to give unidentified oligomers in all of the reactions. Tetrathiocin **1** also reacted in chloroform/acetonitrile solution to give the ring-expansion product **3** in 76% yield after 4.5 h, whereas no change was observed in chloroform solution. Sixteen-membered cyclic compound **3** was also obtained from the chloroform/methanol solution (1:4) of **1**, although the yield was low (15%) and the main products were polymeric materials ($\approx$60%). A 1,2-dithiete, expected to be formed by the reaction of **1** under the conditions, was not detected. In the reaction of **6**, a reaction mechanism which involved intermediates **13** and **14** could not be completely ruled out. However, another mechanism is required at least for the reactions of **8**, **9**, and **1**. The reaction of tetrathiocin **8** is considered to proceed via nucleophilic attack on **8** by acetonitrile to form the zwitter ion intermediate **17**,
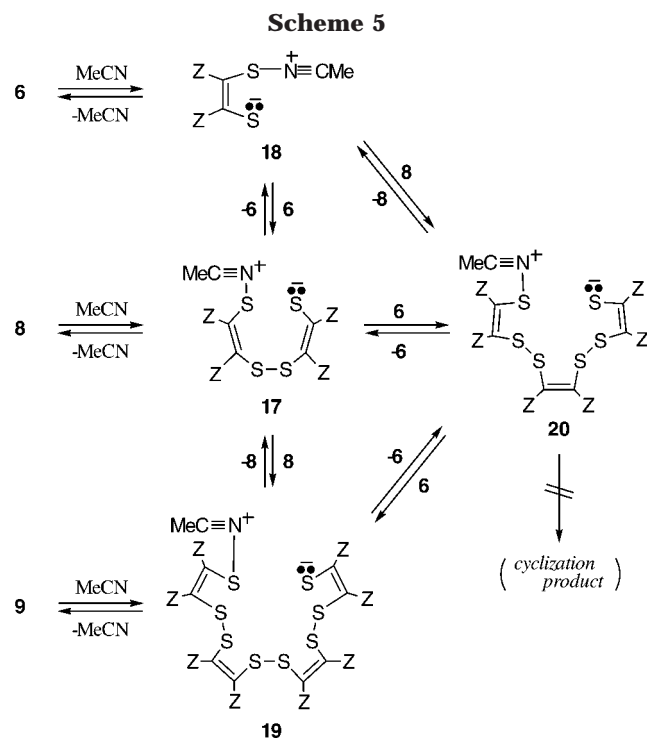
Scheme 5

Scheme 6

as shown in Scheme 5. Intramolecular cyclization of **17** gives zwitter ion **18** with the extrusion of 1,2-dithiete **6**. The intermediate **18** also yields **6** by further intramolecular cyclization. Nucleophilic addition of **17** to another tetrathiocin **8** followed by cyclization forms 16-membered cyclic compound **9** via intermediate **19**. Another path for **9** from **8** involves two additions of **6** to **17** via intermediate **20**. A 12-membered cyclic product was not obtained in any reaction. This fact can be explained on the basis of the unfavorable configuration of **20** in the cyclization reaction. The other reactions of **6**, **9**, and **1** are believed to proceed through similar mechanisms. An increase in the formation of potentially unfavorable tetrathiocin **8** compared to the product ratio in the reaction of **6** in chloroform or benzene might be due to intramolecular anion−cation interaction in zwitter ion **17**, which leads to the desired intramolecular cyclization.

Unsaturated cyclic compounds with disulfide units **6**, **8**, and **9** were also found to react on silica gel in a 2D-TLC study. When a chloroform solution of **6** was stirred for 4 h in the presence of silica gel, tetrathiocin **8** was obtained as a main product (45%) together with 16-membered cyclic compound **9** in 24% yield (Scheme 6). Tetrathiocin **8** and 16-membered heterocycle **9** also reacted in chloroform solution in the presence of silica gel: compounds **6** (5.3%) and **9** (42%) were formed from **8**, and **6** (10%) and **8** (40%) from **9**, respectively, after 4 h. Although the mechanism of these reactions on the surface of silica gel has not yet been clarified, the material balance of the products is different from the
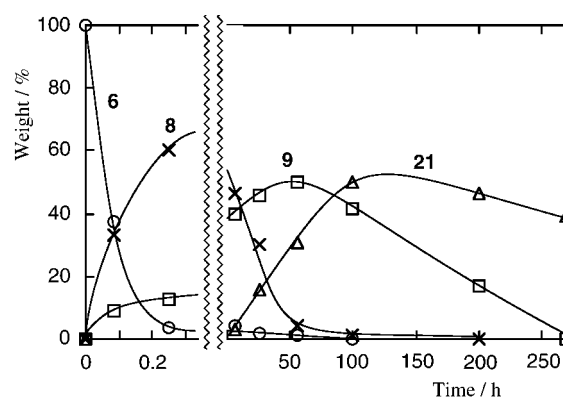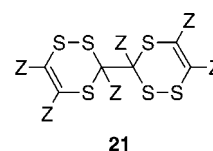

Figure 4. Time−course diagram of the reaction of **6** in chloroform in the presence of silica gel.

reaction of **6** without silica gel. The long reaction time led to the formation of bicyclic product **21** (54% GPC yield

after 4 d from dithiete **6**), and a compound of this type **2** has been obtained by the oxidation of disodium *cis*-ethene-1,2-dithiolate. A time−course study showed that tetrathiocin **8** and then tetramer **9** were formed in the reaction of **6**, as shown in Figure 4. Finally, the formation of **21** increased with the disappearance of tetramer **9**. This result indicates that tetramer **9** was formed stepwise via tetrathiocin **8** in the presence of silica gel. In addition, bicyclic compound **21** may be formed by intramolecular double cyclization via an open-chain 12-membered intermediate on the silica gel surface.

Theoretical Study of Ring-Size Selectivity in Ring Conversion of 1,2-Dithiete and Related Compounds. A 12-membered cyclic compound was not obtained in any of the ring conversion reactions and oxidations of dithiolate and dithiolene complexes. This lack of formation of a 12-membered cyclic compound may be due to the unfavorable configuration in the ring closure reaction. We tried to compare the relative energy of a 12-membered cyclic compound with those of 4-, 8-, and 16-membered cyclic compounds using ab initio molecular orbital calculations, since the configuration in the ring closure reaction is considered to be strongly influenced by the conformation and strain of the products. Some theoretical studies have been made for 1,2-dithiete.[21] The structures of dithiete **22**, tetrathiocin **1**, 12-
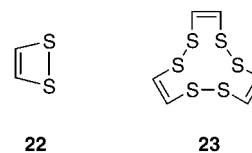
membered cyclic compound **23**, and 16-membered macrocycle **3** were calculated as model molecules using the Hartree−Fock (HF) method with a 6-31G* basis set. The

(20) (a) Diehl, F.; Meyer, H.; Schweig, A.; Hess, B. A., Jr.; Fabian, J. *J. Am. Chem. Soc.* **1989**, *111*, 7651. (b) Rodler, M.; Bauder, A. *Chem. Phys. Lett.* **1985**, *114*, 575. (c) Schulz, R.; Schweig, A.; Hartke, K.; Koster, J. *J. Am. Chem. Soc.* **1983**, *105*, 4519.
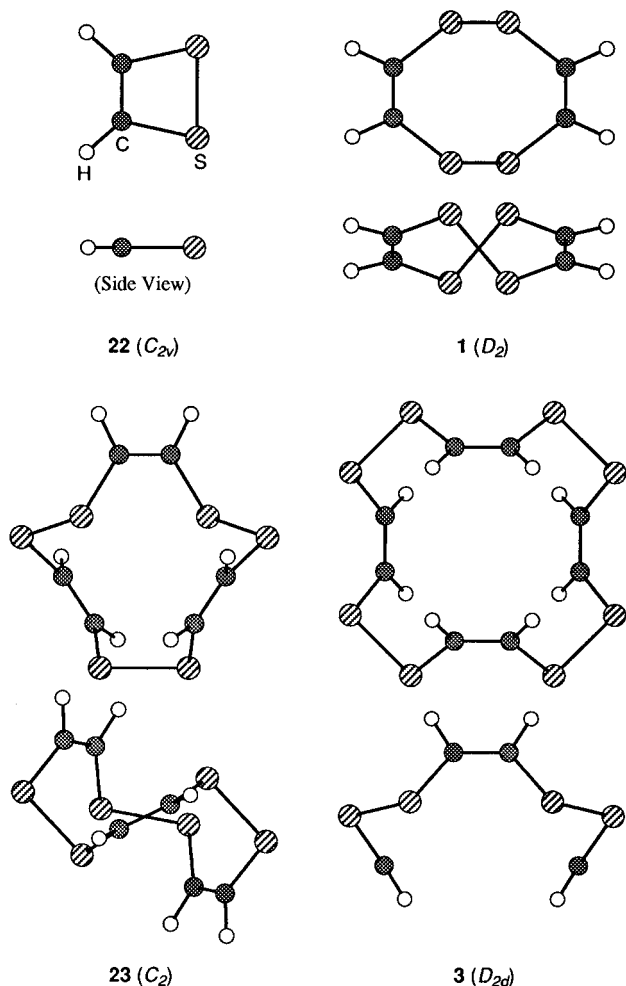
Figure 5. Optimized geometries of unsaturated cyclic compounds possessing disulfide units by the HF method with the 6-31G* basis set.

Figure 6. Relative energies (kcal mol^{-1}) for a $C_2H_2S_2$ unit of **22**, **1**, **23**, and **3** based on MP2 energies for the HF geometries.

of corresponding molecule chains, and this effect is believed to be greater in longer chains, it is reasonable that the lack of formation of a 12-membered cyclic compound is due to a configurational disadvantage. To clarify the ring-size selectivity correctly, more detailed theoretical study of geometries and energies of the open-chain intermediates and the transition states is required at least for the reactions which mechanisms could be presumed, and it is our next subject matter.

Conclusion

A 4-membered heterocyclic unsaturated compound, 3,4-bis(methoxycarbonyl)-1,2-dithiete, was synthesized and isolated by oxidation of the corresponding titanocene dithiolene complex with sulfuryl chloride, and its structure was characterized by X-ray crystallographic analysis, which showed an almost planar geometry. The dimeric and tetrameric cyclic compounds with similar bonding characteristics were also obtained by oxidation of disodium *cis*-ethene-1,2-dithiolate or titanocene dithiolene complexes. The 4-, 8-, and 16-membered unsaturated cyclic compounds with disulfide bonds were found to undergo ring conversion reactions with each other under various conditions. The ring-size selectivity of these reactions was clarified by a study of the mechanism of ring conversion and by ab initio molecular orbital calculations of the cyclic molecules.

Experimental Section

General Methods. Ether, tetrahydrofuran, and benzene were distilled from sodium metal before use. Chloroform and acetonitrile were distilled from calcium hydride and stored with 4A molecular sieves. Methanol and ethanol were distilled from the magnesium cake and also stored with 4A molecular sieves. Gel permeation chromatography (GPC) was performed using a JAI LC-08 and a LC-908 liquid chromatograph with two JAIGEL-1H columns (20 mm × 600 mm), and the products were eluted with chloroform.

Oxidation of Disodium *cis*-Ethene-1,2-dithiolate with Iodine. An aqueous solution (150 mL) of disodium *cis*-ethene-1,2-dithiolate[10] (2.78 g, 20.4 mmol), prepared from *cis*-1,2-bis-(benzylthio)ethene and sodium, and iodine (5.18 g, 20.4 mmol) in 20% aqueous potassium iodide (150 mL)[22] were added consecutively from two dropping funnels with vigorous stirring at −10 °C under nitrogen to a heterogeneous solution of ether (300 mL) and water (250 mL) over 7 h. After additional stirring for 1 h, the products were extracted with ether (100 mL × 2) and washed with 10% sodium thiosulfate solution (100 mL × 2) and water (150 mL × 2). The solution was dried over magnesium sulfate. After removal of the solvent in vacuo, purification by a short cellulose column chromatography (chloroform) followed by gel permeation chromatography (chloroform) gave 1,2,5,6-tetrathiocin (**1**) (254 mg), 3,3′-bi(3*H*-1,2,4-trithiinyl) (**2**) (*meso/dl* = 2/5) (9.6 mg), and (*Z,Z,Z,Z*)-

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1,2,5,6,9,10,13,14-octathiacyclohexadeca-3,7,11,15-tetraene (**3**) (32 mg) in 14, 0.5, and 2.0% yields, respectively. Spectral data for **1**, *meso*-**2**, and **3** have been already reported in the preliminary communication.[6]

dl-3,3′-Bi(3*H*-1,2,4-trithiinyl) (*dl*-2). From spectra of the *dl*- and *meso*-mixture: ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.96 (s, 2H), 6.61 (d, 2H, J = 9.8 Hz), 6.76 (d, 2H, J = 9.8 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 56.1, 115.4, 126.5.

Oxidation of Disodium *cis*-1,2-Bis(methoxycarbonyl)-ethene-1,2-dithiolate with Iodine. To a brown tetrahydrofuran solution (200 mL) of disodium *cis*-1,2-bis(methoxycarbonyl)ethene-1,2-dithiolate, prepared in situ from titanocene dithiolene complex **4**[12] (382 mg, 0.99 mmol) and sodium methoxide (108 mg, 1.99 mmol) in methanol (20 mL), was added a tetrahydrofuran solution (200 mL) of iodine (253 mg, 1.00 mmol) over 6 h under nitrogen. After removal of the solvent in vacuo, chloroform (100 mL) was added to the residue. The solution was washed with 10% sodium thiosulfate solution (100 mL × 2) and water (100 mL × 2). The solution was dried over magnesium sulfate. After removal of the solvent, purification by gel permeation chromatography (chloroform) gave 2,3,5,6-tetrakis(methoxycarbonyl)-1,4-dithiin (**5**) (79 mg) in 39% yield: mp 123 °C (dec; lit. 126 °C);[23] ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.85 (s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 53.6, 134.6, 161.7.

Oxidation of [1,2-Bis(methoxycarbonyl)ethene-1,2-dithiolato]bis(π-cyclopentadienyl)titanium(IV) (4) with Sulfuryl Chloride. To a benzene solution (350 mL) of titanocene dithiolene complex **4**[12] (586 mg, 1.52 mmol), prepared from titanocene pentasulfide[24] and dimethyl acetylenedicarboxylate, was added a benzene solution (150 mL) of sulfuryl chloride (2.04 g, 15.1 mmol). After additional stirring for 5 min, water (250 mL) was added to the solution and stirring was continued for 30 min. The products were extracted with benzene (50 mL × 2), and the solution was dried over magnesium sulfate. After removal of the solvent in vacuo, purification by gel permeation chromatography (chloroform) gave 3,4-bis(methoxycarbonyl)-1,2-dithiete (**6**) (163 mg), 3,4,7,8-tetrakis(methoxycarbonyl)-1,2,5,6-tetrathiocin (**8**) (4.0 mg), and (*Z,Z,Z,Z*)-3,4,7,8,11,12,15,16-octakis(methoxycarbonyl)-1,2,5,6,9,-10,13,14-octathiacyclohexadeca-3,7,11,15-tetraene (**9**) (5.0 mg) in 66, 1.6, and 2.0% yields, respectively.

3,4-Bis(methoxycarbonyl)-1,2-dithiete (6): mp 83.5−84.0 °C (pale yellow plates, chloroform−hexane); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.87 (s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 52.6, 131.5, 157.1; IR (KBr) ν_{max} 2960, 1730, 1540, 1510, 1430, 1240, 1000 cm^{-1}; UV (cyclohexane) λ_{max} 214 (ϵ 3.4 × 10^3), 249 (ϵ 2.5 × 10^3), 287 (ϵ 1.3 × 10^4) nm; MS (EI): m/z 206 (M$^+$), 178, 88, 59. Anal. Calcd for C$_6$H$_6$O$_4$S$_2$: C, 34.94; H, 2.93. Found: C, 35.19; H, 2.79.

3,4,7,8-Tetrakis(methoxycarbonyl)-1,2,5,6-tetrathiocin (8): mp 133.5−134.0 °C (yellow prisms, chloroform); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.86 (s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 53.8, 136.5, 163.6; IR (KBr) ν_{max} 2960, 1730, 1540, 1510, 1430, 1240, 1000 cm^{-1}; UV (cyclohexane) λ_{max} 215 (ϵ 8.3 × 10^3), 275 (ϵ 6.7 × 10^3), 305 (ϵ 4.9 × 10^3), 372 (ϵ 3.2 × 10^3) nm; MS (FAB): m/z 414 (M$^+$ + 2), 412 (M$^+$), 348, 206, 178. Anal. Calcd for C$_{12}$H$_{12}$O$_8$S$_4$: C, 34.94; H, 2.93. Found: C, 35.37; H, 2.91.

(*Z,Z,Z,Z*)-3,4,7,8,11,12,15,16-Octakis(methoxycarbonyl)-1,2,5,6,9,10,13,14-octathiacyclohexadeca-3,7,11,15-tetraene (9): mp 96 °C (dec, pale yellow solid); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.85 (s); ^{13}C NMR (100 MHz, CDCl$_3$) δ 53.5, 140.1, 162.1; IR (KBr) ν_{max} 2960, 1730, 1540, 1430, 1240, 1000 cm^{-1}; UV (chloroform) λ_{max} 292 (ϵ 2.3 × 10^4) nm; MS (EI): m/z 206 (M$^+$/4), 178, 88, 59; cryoscopy (benzene), M_r = 849. Anal. Calcd for C$_{24}$H$_{24}$O$_{16}$S$_8$: C, 34.94; H, 2.93. Found: C, 35.21; H, 3.11.

Oxidation of [(Methoxycarbonyl)ethene-1,2-dithiolato]bis(π-cyclopentadienyl)titanium(IV) (10) with Sulfuryl Chloride. Oxidation of titanocene dithiolene complex **10**[25] (653 mg, 2.00 mmol), prepared from titanocene pentasulfide[24]

and dimethyl acetylenedicarboxylate, with sulfuryl chloride under the conditions similar to oxidation of **4** gave 3,7-bis-(methoxycarbonyl)-1,2,5,6-tetrathiocin (**11**) (59 mg) and 3,8-bis(methoxycarbonyl)-1,2,5,6-tetrathiocin (**12**) (44 mg) in 22 and 17% yields, respectively.

3,7-Bis(methoxycarbonyl)-1,2,5,6-tetrathiocin (11): mp 126.0−127.0 °C (yellow plates, chloroform−hexane); ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.86 (s, 6H), 8.12 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 53.1, 130.1, 141.8, 163.1; IR (KBr) ν_{max} 3020, 3000, 2940, 1720, 1510, 1430, 1240, 1020 cm^{-1}; MS (EI) m/z 296 (M$^+$), 332, 212, 180, 148; HRMS calcd for C$_8$H$_8$O$_4$S$_4$ 295.9306, found 295.9303.

3,8-Bis(methoxycarbonyl)-1,2,5,6-tetrathiocin (12): yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.86 (s, 6H), 7.94 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 53.2, 132.7, 137.7, 163.1; IR (KBr) ν_{max} 3030, 3000, 2950, 1710, 1520, 1430, 1230, 1030 cm^{-1}; MS (EI) m/z 296 (M$^+$), 332, 212, 180, 148; HRMS calcd for C$_8$H$_8$O$_4$S$_4$ 295.9306, found 295.9326.

Typical Procedure for Ring Conversion Reaction. A solution (30 mL) of unsaturated cyclic compound possessing disulfide units (41.2 mg) was stirred at room temperature for suitable period under nitrogen. After removal of the solvent in vacuo, purification was carried out by gel permeation chromatography (chloroform).

Reaction of 6 in chloroform for 4 h: 60% conversion; **8** (4.8%); **9** (71%).

Reaction of 6 in benzene for 4 h: 46% conversion; **8** (6.1%); **9** (74%).

Reaction of 6 in chloroform/acetonitrile (1:4) for 2 h: 97% conversion; **8** (19%); **9** (41%).

Reaction of 8 in chloroform/acetonitrile (1:4) for 2 h: 64% conversion; **6** (13%); **9** (44%).

Reaction of 8 in chloroform/ethanol (1:4) for 2 h: 7% conversion; **6** (trace); **9** (74%).

Reaction of 9 in chloroform/acetonitrile (1:4) for 2 h: 45% conversion; **6** (5.8%); **8** (12%).

Reaction of 1 in chloroform/acetonitrile (1:4) for 4.5 h: 80% conversion; **3** (76%).

Reaction of 1 in chloroform/methanol (1:4) for 4.5 h: 100% conversion; **3** (15%).

Typical Procedure for Ring Conversion Reaction in the Presence of Silica Gel. A chloroform solution (30 mL) of the cyclic compound (41.2 mg) in the presence of silica gel (3.0 g) was stirred at room temperature for 4 h under nitrogen. After removal of the silica gel by filtration followed by concentration, purification was carried out by gel permeation chromatography (chloroform).

Reaction of 6: 95% conversion; **8** (45%); **9** (24%).

Reaction of 8: 51% conversion; **6** (5.3%); **9** (42%).

Reaction of 9: 27% conversion; **6** (10%); **8** (40%). The time−course study of the reaction of **6** in the presence of silica gel was achieved by gel permeation chromatography (chloroform) analysis using octadecane as an internal standard.

Reaction of 6 for 4 d: 100% conversion; **8** (0.8%); **9** (45%); **21** (54%).

3,3′-Bi[3*H*-3,5,6-tris(methoxycarbonyl)-1,2,4-trithiinyl] (21). This was produced as a mixture of the *dl*- and *meso*-isomers (≈1/1): yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.81 (s, 6/2H), 3.82 (s, 6/2H), 3.849 (s, 6/2H), 3.853 (s, 6/2H), 3.87 (s, 6/2H), 3.95 (s, 6/2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 53.1 (duplicate), 53.3, 53.7, 54.5, 55.0, 75.2, 77.2, 127.1, 130.6, 146.2 (duplicate), 159.7 (duplicate), 162.2, 164.0, 168.2, 168.4; IR (neat) ν_{max} 2970, 1730, 1600, 1560, 1440, 1250, 1090, 1020 cm^{-1}; MS (EI) m/z 618 (M$^+$), 587, 555, 523, 309, 277; HRMS calcd for C$_{18}$H$_{18}$O$_{12}$S$_6$ 617.9123, found 617.9057.

X-ray Analysis. General Method. Each crystal was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.710 69 Å) on a Mac Science MXC18 diffractometer equipped with a graphite crystal, incident beam monochromator. Cell constants and an orientation matrix for

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data collection were obtained from least-squares refinement. The data were collected at a temperature of 25 ± 1 °C using the $\omega - 2\theta$ scan technique. The scan rate varied from 0 to 5 °/min (in ω). Lorentz and polarization corrections were applied to the data. No absorption correction was made. An extinction correction was not necessary. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares, where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as 1.0 for all observed reflections.

Compound 6. A pale yellow plate of $C_6H_6O_4S_2$ having approximate dimension of $0.30 \times 0.20 \times 0.10$ mm^3 was used: monoclinic space group $P2_1/a$ with $a = 13.549(2)$ Å, $b = 6.885$-(2) Å, $c = 9.398(2)$ Å, $\beta = 101.47(2)°$, $V = 859.2(3)$ Å^3, $Z = 4$, and ρ(calcd) $= 1.594$ g cm^{-3}. Of the 1693 unique data, the 1073 with $I > 3\sigma(I)$ were used in the least-squares refinement to yield $R = 0.063$ and $R_w = 0.064$.

Compound 8. A yellow prism of $C_{12}H_{12}O_8S_4$ having approximate dimension of $0.50 \times 0.40 \times 0.20$ mm^3 was used: triclinic space group $P\bar{1}$ with $a = 17.184(4)$ Å, $b = 12.032(3)$ Å, $c = 9.467(5)$ Å, $\alpha = 113.11(3)°$, $\beta = 105.93(3)°$, $\gamma = 80.44$-(2)°, $V = 1727.4(12)$ Å^3, $Z = 4$, and ρ(calcd) $= 1.585$ g cm^{-3}. Of the 7414 unique data, the 6226 with $I > 3\sigma(I)$ were used in the least-squares refinement to yield $R = 0.045$ and $R_w = 0.076$.

Compound 11. A yellow plate of $C_8H_8O_4S_4$ having approximate dimension of $0.35 \times 0.35 \times 0.20$ mm^3 was used: orthorombic space group $Pcn2$ with $a = 8.297(7)$ Å, $b = 18.405$-(7) Å, $c = 7.693(4)$ Å, $V = 1174.9(10)$ Å^3, $Z = 4$, and ρ(calcd) $= 1.675$ g cm^{-3}. Of the 3117 unique data, the 2573 with $I > 3\sigma$-(I) were used in the least-squares refinement to yield $R = 0.037$ and $R_w = 0.037$.

Theoretical Study. Geometries were optimized using the Hartree−Fock (HF) method with the 6-31G* basis set. The final energies were calculated by the second-order Møller−Plesset perturbation (MP2) method (frozen-core), using the HF geometries. All calculations were performed by using the Gaussian94 program on an IBM RS/6000 computer.

Supporting Information Available: Detailed information of the X-ray crystallographic analyses of **6**, **8**, and **11**, including structure diagrams, details of data collection and reduction and structure solution and refinement, and tables of positional and thermal parameters, bond lengths and angles, and torsional angles, and structure diagrams, Cartesian coordinates, and final (MP2; frozen-core) energies of molecules **22**, **1**, **23**, and **3** calculated by the HF method with the 6-31G* basis set (42 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.