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1,2,3,4,5,6,7,8-Octathionane, a Novel Cyclic Polysulfide. Synthesis and Crystal Structure†

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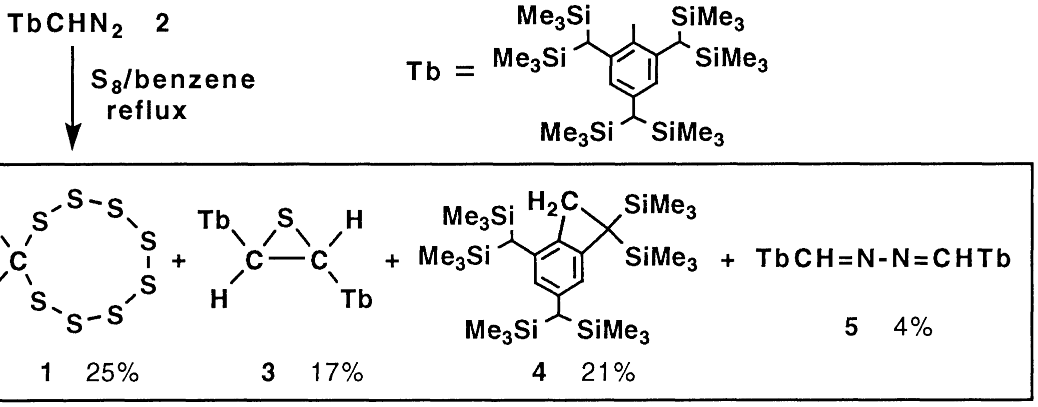
Thermal reaction of a sterically bulky diazomethane with elemental sulfur in benzene afforded a novel cyclic polysulfide, 1,2,3,4,5,6,7,8-octathionane (**1**). Molecular structure of **1** was determined by X-ray crystallographic analysis and the geometry of its CS_8 ring of **1** was compared with that of the theoretically optimized cyclononasulfur (S_9).

During the last years the chemistry of cyclic polysulfides has been of great interest and widely explored from the standpoints of not only their unique structures and reactivities but also their biological activities.1) However, there exist few examples of stable cyclic polysulfides of C_xS_y type containing more sulfurs2) than the well-known 1,2,3,4,5-pentathiepin derivatives (C_2S_5 ring system) in contrast to the extensive studies on the synthesis and molecular geometry of a variety of cyclopolysulfurs.3) Recently, we have succeeded in the synthesis of novel cyclic tetrachalcogenides containing group 14 metals such as $Tb(Ar)MY_4$ (M=Si, Ge, Sn; Y=S, Se; Ar=mesityl or 2,4,6-triisopropylphenyl)4) by taking advantage of a new and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tb in this paper).5)

In this communication, we describe the first synthesis of stable 1,2,3,4,5,6,7,8-octathionane **1** by the thermal reaction of Tb-substituted diazomethane **2**6) with elemental sulfur, and also report the crystallographic structure analysis of this unprecedented nine-membered cyclic polysulfide **1**.7)



When a benzene solution (35 ml) of $TbCHN_2$ (**2**; 565 mg, 0.955 mmol) was added dropwise into a refluxing benzene solution (20 ml) of an excess amount of elemental sulfur (2.44 g, 9.57 mmol as S_8) during 2 h

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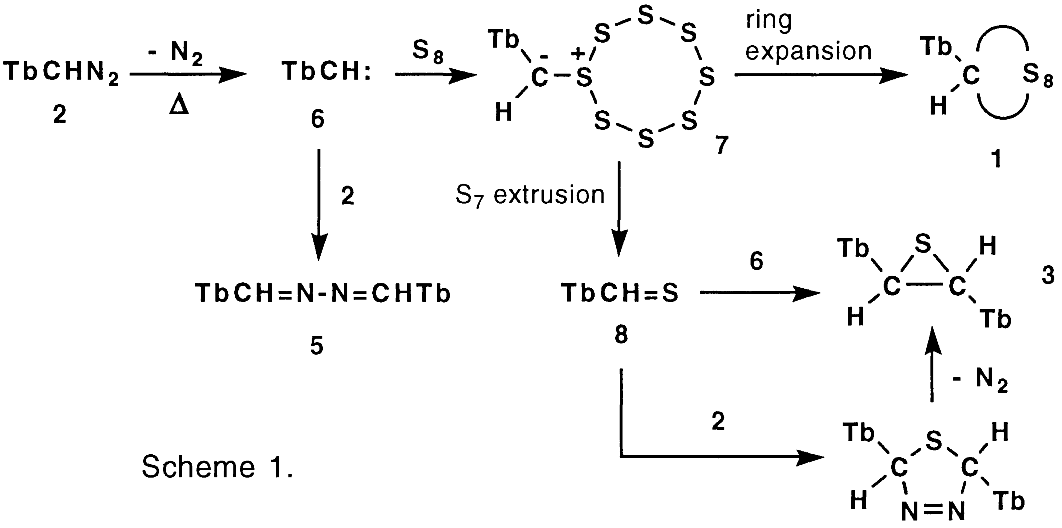
†Dedicated to Professor Emeritus Osamu Simamura of The University of Tokyo on the occasion of his 80th birthday.

and the reaction mixture was refluxed for further 4 h, octathionane **1** (191.8 mg, 25%) and episulfide **3** (93.0 mg, 17%) were isolated as sulfurization products along with benzocyclobutane **4** (111 mg, 21%) and azine **5** (23 mg, 4%). The products were isolated by removal of excess sulfur by recrystallization and subsequent exhaustive chromatographic separation (HPLC and TLC).[8] On the other hand, in the absence of sulfur, diazomethane **2** was thermally decomposed in refluxing benzene for 4 h to give the benzocyclobutane **4** (55%), which was undoubtedly formed by the thermal denitrogenation of **1** followed by an intramolecular C-H insertion of the resulting carbene **6** toward the *ortho*-bis(trimethylsilyl)methyl group, together with azine **5** (6%).

$$\underset{\mathbf{2}}{\mathrm{TbCHN_2}} \xrightarrow[\text{benzene reflux}]{} \underset{55\%}{\mathbf{4}} + \underset{\mathbf{5}\quad 6\%}{\mathrm{TbCH{=}N{-}N{=}CHTb}}$$

The mechanism of formation of **1** and **3** in the reaction of **2** with sulfur can be interpreted in terms of the initial addition of intermediary carbene **6** to cyclooctasulfur followed by the competitive ring expansion and S_7 extrusion of the resulting sulfonium ylide **7** leading to the octathionane **1** and thioaldehyde **8**, respectively. Episulfide **3**, the configuration of which is tentatively assigned as *trans* for steric reason, might be formed by the reaction of thioaldehyde **8** and co-existing carbene **6** and/or diazomethane **2**, as shown in Scheme 1.



Scheme 1.

All the products described here were isolated in a stable crystalline form and showed satisfactory spectral and analytical data.[9] The octathionane **1** was stable in refluxing benzene or $EtOH\text{-}CHCl_3$ and its single crystal for X-ray diffraction structure analysis was obtained by recrystallization. The refined final molecular structure of **1** is shown in Fig. 1 together with the selected interatomic bond lengths and angles.[10]

Since S_9 among S_6-S_{12} is the only sulfur ring whose geometry has not been experimentally determined, the structure analysis of **1** is worthy of note from the viewpoint of not only the first example of an octathionane derivative but also a comparative study on the structure of nine-membered cyclopolysulfide rings. As shown in Fig. 1, the octathionane ring of **1** has C_1 symmetry in contrast to a cyclononasulfur (S_9) ring with theoretically optimized C_2 symmetry[3] probably due to the steric repulsion between the bulky Tb group and the polysulfur linkage.

Indeed, MMP2 calculations have revealed that replacement of one sulfur atom of S_9 by TbCH unit gives the lowest converged ground state geometry with no symmetry factor which is almost identical with the crystal structure of **1**.[11] However, the geometry of the polysulfur linkage, *i. e.* the atom stacking mode of octathionane ring moiety, essentially resembles that of S_9, and the S-S bonds are neither unusually long or short as in the case of calculated S_9 molecule. Further investigation on the reactivities of this novel cyclopolysulfide **1** is currently in progress.

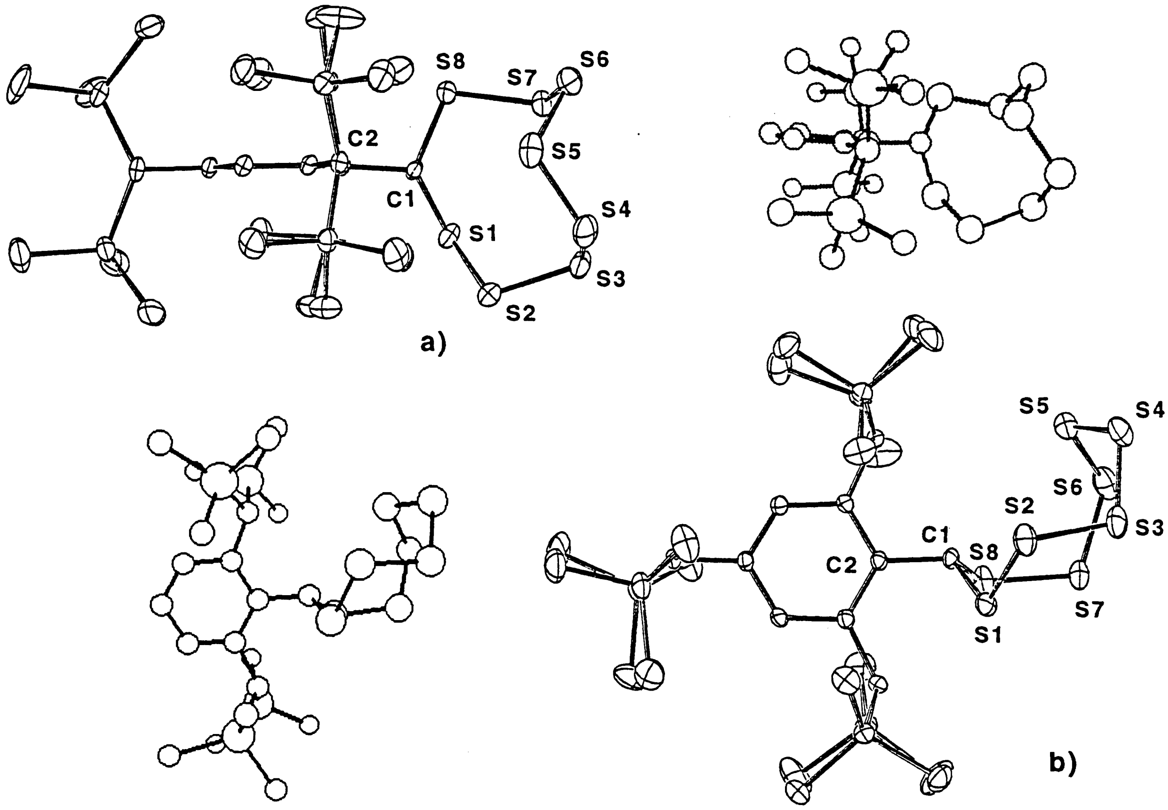


Fig. 1. *ORTEP* drawings of $TbCHS_8$ (**1**) together with the optimized structure of **1** exclusive of *p*-$(Me_3Si)_2CH$ group by MMP2 calculation; a) top view, b) side view; selected bond lengths (Å) and angles (deg); S1-S2, 2.022(3); S2-S3, 2.045(3); S3-S4, 2.029(3); S4-S5, 2.034(4); S5-S6, 2.046(4); S6-S7, 2.066(4); S7-S8, 2.016(3); C1-S1, 1.831(7); C1-S8, 1.845(6); C1-C2, 1.519(9); C1-S1-S2, 105.9(2); S1-S2-S3, 108.4(2); S2-S3-S4, 108.6(2); S3-S4-S5, 108.7(2); S4-S5-S6, 109.1(2); S5-S6-S7, 106.0(2); S6-S7-S8, 108.4(2); S7-S8-C1, 104.7(2); S8-C1-S1, 111.9(3); C2-C1-S1, 115.9(4); C2-C1-S8, 108.9(4).

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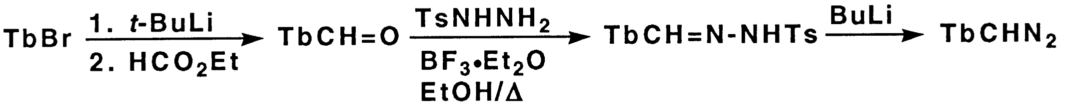
6) Diazomethane **2** was readily prepared by the conventional method starting from TbBr as follows.



$$\mathrm{TbBr}\xrightarrow[\text{2. }\mathrm{HCO_2Et}]{\text{1. }t\text{-BuLi}}\mathrm{TbCH{=}O}\xrightarrow[\mathrm{BF_3{\bullet}Et_2O},\ \mathrm{EtOH}/\Delta]{\mathrm{TsNHNH_2}}\mathrm{TbCH{=}N{-}NHTs}\xrightarrow{\mathrm{BuLi}}\mathrm{TbCHN_2}$$

7) The formation of 9,9-dimethyl-1,2,3,4,5,6,7,8-octathionane was demonstrated by HPLC analysis though not isolated; R. Steudel, R. Strauss, and D. Jensen, *Chem.-Ztg.*, **109**, 349 (1985).

8) HPLC; LC-908(Japan Analytical Industry Co., Ltd.)/JAIGEL-1H and -2H/$CHCl_3$, TLC; silical gel/hexane.

9) **1**; yellow crystals, mp 200.5-201.5 °C (dec); ^{1}H-NMR(500 MHz, $CDCl_3$, 82 °C) δ 0.08(s, 18H), 0.12(s, 18H), 0.14(s, 18H), 1.38(s, 1H), 2.04(s, 1H), 2.16(s, 1H), 6.34(brs, 1H, -S-C$\underline{\text{H}}$(Tb)-S-), 6.41(s, 1H), 6.45(s, 1H); ^{13}C-NMR(125 MHz, $CDCl_3$, 80 °C) δ 0.9(q), 1.7(q), 1.8(q), 26.0(d), 27.8(d), 31.1(d), 67.7(d), 123.6(d), 125.6(s), 127.8(d), 144.5(s), 144.7(s), 146.6(s); Anal. found C; 41.10, H; 7.11, S; 31.36%, calcd for $C_{28}H_{60}S_8Si_6$ C; 40.92, H; 7.36, S; 31.21%. **3**; white crystals, mp 224.5-226.0 °C; ^{1}H-NMR(500 MHz, $CDCl_3$) δ 0.03(s, 18H), 0.06(s, 36H), 0.09(s, 18H), 0.10(s, 36H), 1.28(s, 2H), 2.02(s, 2H), 2.30(s, 2H), 4.39(s, 2H), 6.31(s, 2H), 6.43(s, 2H); ^{13}C-NMR(125 MHz, $CDCl_3$, 57 °C) δ 0.5(q), 1.0(q), 1.5(q), 2.0(q), 25.9(dx2), 29.9(d), 48.3(d), 123.0(d), 128.1(d), 130.3(s), 140.3(s), 140.5(s), 146.4(s); Anal. found C; 57.65, H; 10.19, S; 3.01%, calcd for $C_{56}H_{120}SSi_{12}$ C; 57.85, H; 10.40, S; 2.76%. **4**; white crystals, mp 213.5-214.5 °C; ^{1}H-NMR(500 MHz, $CDCl_3$) δ -0.04(s, 18H), 0.01(s, 18H), 0.02(s, 18H), 1.29(s, 1H), 1.33(s, 1H), 2.77(s, 2H), 6.23(s, 2H); ^{13}C-NMR(125 MHz, $CDCl_3$) δ -1.6(q), 0.4(q), 0.6(q), 23.0(d), 30.5(d), 31.3(s), 31.9(t), 115.5(d), 125.0(d), 135.1(s), 137.0 (s), 141.8(s), 150.4(s); Anal. found C; 59.19, H; 10.43%, calcd for $C_{28}H_{60}Si_6$ C; 59.49, H; 10.70%. **5**; white crystals, mp >300 °C; ^{1}H-NMR(500 MHz, $CDCl_3$) δ 0.02(s, 72H), 0.06(s, 36H), 1.37(s, 2H), 2.42(s, 2H), 2.67(s, 2H), 6.34(s, 2H), 6.47(s, 2H), 8.77(s, 2H); ^{13}C-NMR(125 MHz, $CDCl_3$) δ 0.5(q), 0.7(q), 24.5(d), 29.7(d), 30.6(d), 122.2(d), 126.5(s), 126.9(d), 144.0(s), 144.2(s), 144.3(s), 163.2(d); Anal. found C; 57.84, H; 10.30, N; 2.51%, calcd for $C_{56}H_{120}N_2Si_{12}$ C; 58.05, H; 10.44, N; 2.42%.

10) Crystal data for **1**; $C_{28}H_{60}S_8Si_6$, MW = 821.78, *monoclinic*, $P2_1/c$, a = 9.951(1), b = 13.075(1), c = 35.076(5) Å, β =97.49(1) °, V = 4544.7(1.0) Å^3, Z = 4, D_c = 1.200 g cm^{-3}, μ = 50.61 cm^{-1}, $R(R_w)$ = 0.092(0.094). A total of 7330 reflections, of which 6561 were unique and 5108 were used, were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Cu Kα radiation (R = 1.5418 Å). The structures were solved by direct method (*MULTAN 78*) using *UNICS III* and refined by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms. The 8 hydrogen atoms were introduced from D-Fourier maps in the course of refinements and the other hydrogen atoms were located at calculated positions.

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