

Structure Elucidation of 6-*t*-Butyl-6-phenylpentathiane Monoxides by X-ray Crystallography and DFT Calculations

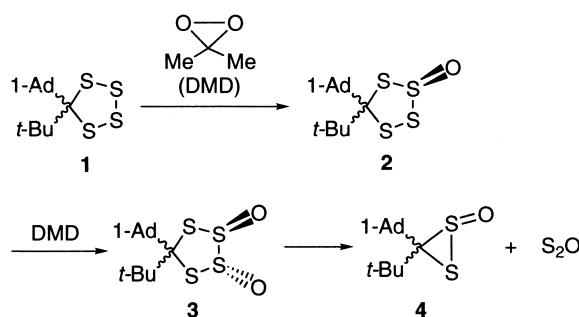
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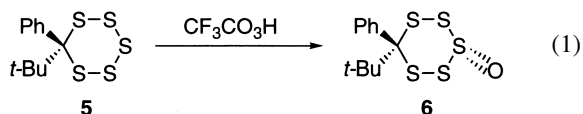
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6-*t*-Butyl-6-phenylpentathiane was oxidized with trifluoroacetic acid ($\text{CF}_3\text{CO}_2\text{H}$) or dimethyldioxirane (DMD) at -20°C . Oxidation with $\text{CF}_3\text{CO}_2\text{H}$ yielded pentathiane 3-oxide as the main product, whereas that of DMD gave 1- and 3-oxides. The structures of 1- and 3-oxides were finally determined by X-ray crystallographic analysis. DFT calculations of the NMR chemical shifts were performed on the chair and twist forms of the pentathiane and sixteen isomers of the monoxides with the GIAO method at the B3LYP/6-31G* level. The calculated chemical shifts were verified to be in practical agreement with the experimental data of the pentathiane and the isolated 1- and 3-oxides.

The oxidation of cyclic polysulfides has been drawing much attention not only due to the fundamental interest in the regio- and stereochemistries^{1–8} compared with acyclic tri- and tetrasulfides^{9,10} but also for the potential of the resulting oxides as precursors of reactive sulfur species.^{2,7,8,11} Recently, we reported on the oxidation reactions of tetrathiolanes and pentathianes; the oxidation of 5-(1-adamantyl)-5-*t*-butyltetrathiolane (**1**) with dimethyldioxirane (DMD) took place first at the 2-position to give the 2-oxide **2**, and then at the 3-position to give the 2,3-dioxide **3**.⁷ Decomposition of the 2,3-dioxide **3** in solution at temperatures higher than -10°C gives rise to the dithiirane 1-oxide **4** and S_2O (Scheme 1). On the other hand,



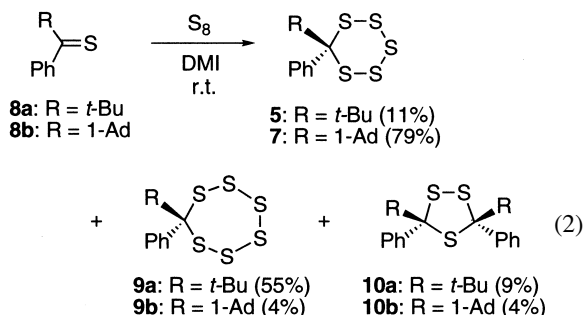
the oxidation of 6-*t*-butyl-6-phenylpentathiane (**5**) with $\text{CF}_3\text{CO}_2\text{H}$ yielded mainly 3-oxide **6** (Eq. 1).⁸ We also preliminarily reported that 3-oxide **6** takes a twist conformation both in the solid state and in solution. Here, we report on details of the structure elucidation of pentathiane monoxides formed by the oxidation of the pentathiane **5** with $\text{CF}_3\text{CO}_2\text{H}$ and DMD based on X-ray crystallography and density functional theory (DFT) calculations.



Results and Discussion

Improved Preparation of Pentathianes. Pentathianes **5**

and **7** were prepared by a method which we reported previously,¹² or by a reaction of the corresponding thioketones **8** with elemental sulfur in 1,3-dimethyl-2,4-imidazolidinone (DMI) at room temperature (Eq. 2). In the latter reaction, **5** and **7** were obtained in improved yields along with hexathiepanes **9** and 1,2,4-trithiolanes **10**. The reaction of **8** with elemental sulfur took place in DMF and DMSO similarly, and did not occur in nonpolar solvents, such as benzene, CHCl_3 , or CS_2 .



An X-ray crystallographic analysis of **5** revealed that it takes a chair conformation in the solid state similarly to the reported pentathianes,¹³ where the phenyl and *t*-butyl groups possess axial and equatorial orientations, respectively (Fig. 1). A dynamic ^1H NMR spectroscopic analysis showed that **5** takes the chair conformation in solution as well.⁸ The cis-substituted structure of 1,2,4-trithiolane **10a** was also determined by X-ray crystallography (Fig. 2). This contrasts with a recent report that both the cis and trans isomers of 3,5-diaryl-3,5-di-*t*-butyl-1,2,4-trithiolanes were obtained by a reaction of the corresponding ketones with Lawesson's reagent in refluxing toluene.¹⁴

Oxidation of Pentathianes **5 and **7** with $\text{CF}_3\text{CO}_2\text{H}$ and DMD.** (i) $\text{CF}_3\text{CO}_2\text{H}$. Pentathiane **5** was oxidized with 2 molar amounts of $\text{CF}_3\text{CO}_2\text{H}$ in CH_2Cl_2 at -20°C to give monoxide **6** in 25% isolated yield.⁸ When **5** was oxidized with 1.4 molar amounts of $\text{CF}_3\text{CO}_2\text{H}$, the ^1H NMR spectrum of the mixture showed the formation of **6** in 41% yield along with unreacted **5** (30%), thioketone *S*-oxide **11a** (1%), and several un-

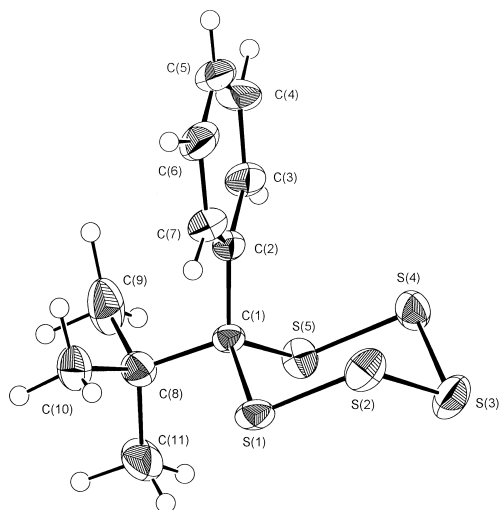


Fig. 1. ORTEP drawing of 6-*t*-butyl-6-phenylpentathiane (**5**) (50% ellipsoidal probability). Selected bond lengths (Å) and angles (deg): C1–S1, 1.856(3); S1–S2, 2.034(2); S2–S3, 2.061(2); S3–S4, 2.057(2); S4–S5, 2.037(2); S5–C1, 1.842(3); C1–C2, 1.525(4); C1–C8, 1.598(4); S2–S1–C1, 103.7(1); S1–S2–S3, 103.9(1); S2–S3–S4, 99.4(1); S3–S4–S5, 103.1(1); S4–S5–C1, 104.5(1), S1–C1–S5, 108.3(2), C2–C1–C8, 112.6(2).

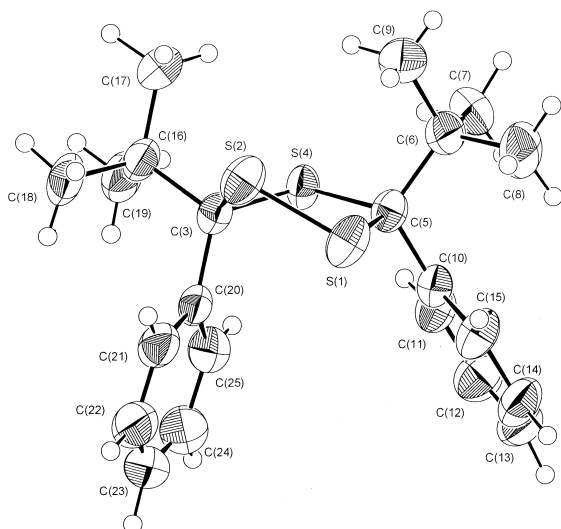


Fig. 2. ORTEP drawing of *cis*-3,5-di-*t*-butyl-3,5-diphenyl-1,2,4-trithiolane (**10a**) (50% ellipsoidal probability). Selected bond lengths (Å) and angles (deg): S1–S1, 2.024(2); S2–C3, 1.831(4); C3–S4, 1.845(4); S4–C5, 1.846(4); C5–S1, 1.863(4); C3–C20, 1.540(5); C3–C16, 1.589(6); C5–C10, 1.530(6); C5–C6, 1.588(6); S1–S2–C3, 94.6(2); S2–C3–S4, 104.1(2); C3–S4–C5, 104.0(2); S4–C5–S1, 106.8(2); C5–S1–S2, 100.3(2); C20–C3–C16, 112.0(3); C10–C5–C6, 111.7(4).

identified compounds. This observation indicates that **6** was formed in at least 58% yield, based on the consumed pentathiane **5** (Eq. 3).

The structure of **6** was finally established by X-ray crystallography to be the 3-oxide (**Fig. 3**).⁸ The 3-oxide **6** takes a twist conformation in the solid state with the oxygen atom *cis* to the *t*-butyl group, which is in contrast with the starting pen-

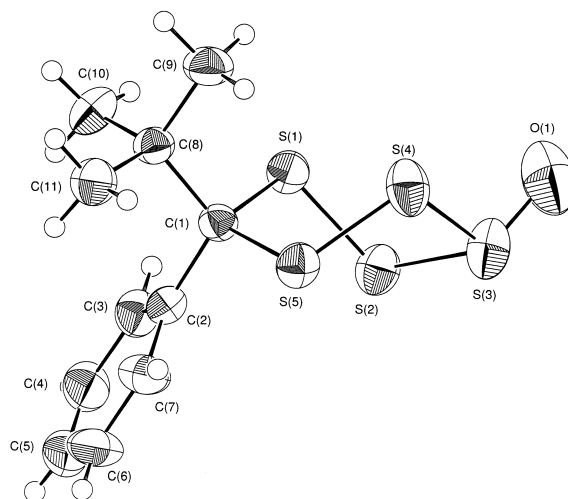
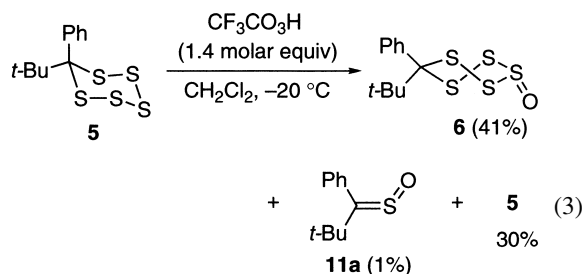
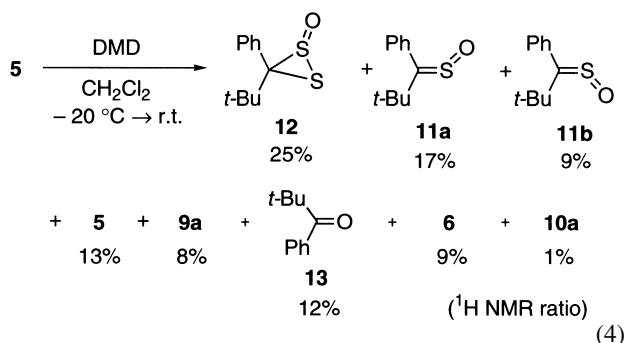


Fig. 3. ORTEP drawing of the 3-oxide **6** (50% ellipsoidal probability). Selected bond lengths (Å) and angles (deg): C1–S1, 1.845(3); S1–S2, 2.008(1); S2–S3, 2.182(1); S3–S4, 2.157(2); S4–S5, 1.999(1); S5–C1, 1.887(3); C1–C2, 1.525(4); C1–C8, 1.585(4); S3–O1, 1.432(4); S2–S1–C1, 102.8(2); S1–S2–S3, 104.7(1); S2–S3–S4, 96.9(1); S2–S3–O1, 113.2(2); S4–S3–O1, 102.7(2); S3–S4–S5, 103.8(1); S4–S5–C1, 105.7(2), S1–C1–S5, 107.6(2), C2–C1–C8, 113.3(3).

tathiane **5**, which takes a chair conformation. It was reported that S₆O takes a chair conformation with the oxygen atom occupying the axial position.¹⁵



(ii) **DMD**. The scope of the oxidation of **5** with DMD was quite different from that with CF₃CO₃H. After pentathiane **5** was treated with an equimolar amount of DMD in CH₂Cl₂ at –20 °C, the mixture was warmed to room temperature. The final products were dithiirane 1-oxide **12**¹¹ (25%), (*E*)- and (*Z*)-thioketone *S*-oxides **11a** (17%) and **11b** (9%), **5** (13%), hexathiepane **9a** (8%), ketone **13** (12%), 3-oxide **6** (9%), 1,2,4-trithiolane **10a** (1%) (Eq. 4). The yields were estimated based on the ¹H NMR integral ratio of the mixture.



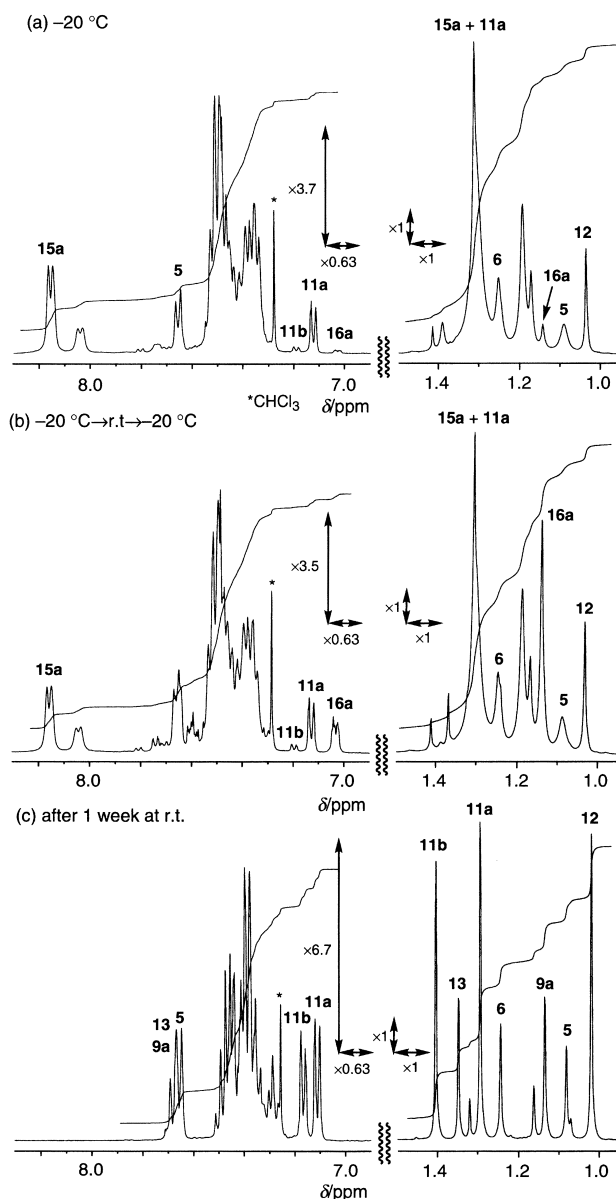
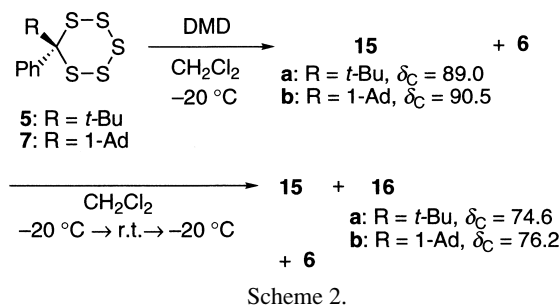


Fig. 4. ^1H NMR spectra of the reaction mixture of pentathiane **5** and DMD: (a) at $-20\text{ }^\circ\text{C}$, (b) $-20\text{ }^\circ\text{C} \rightarrow \text{r.t.}$ (15 min) $\rightarrow -20\text{ }^\circ\text{C}$, (c) after standing at r.t. for 1 week.

The oxidation of **5** with DMD was followed by ^1H and ^{13}C NMR spectroscopies to detect any intermediates. After a treatment with DMD at $-20\text{ }^\circ\text{C}$ for 1 h, volatile materials, including the unreacted DMD, were removed in vacuo below $-20\text{ }^\circ\text{C}$, and the residue was subjected to NMR spectroscopy (Fig. 4). In the ^1H NMR measured at $-20\text{ }^\circ\text{C}$ (Fig. 4a), new signals due to *t*-butyl groups were observed at $\delta = 1.31$ (45%, **15a**), 1.19 (17%), and 1.13 (2%, **16a**), along with known signals due to 3-oxide **6** (9%), dithiirane 1-oxide **12**, and sulfines **11a** and **11b**. In the aromatic region, a characteristic doublet, isolated from the other signals, appeared at $\delta = 8.16$ (d, $J = 6.3\text{ Hz}$, *ortho*-phenyl). Based on the intensity, the doublet seemed to be assigned to **15a**. In the ^{13}C NMR, a pentathiane carbon due to **15a** appeared at $\delta = 89.0$. The mixture was warmed to room temperature, left standing at room temperature for 15



min, and again cooled to $-20\text{ }^{\circ}\text{C}$. The main signals due to **15a** then became weak and, instead, signals due to an alternative intermediate (**16a**) became strong at $\delta = 1.13$ (*t*-Bu) and 7.03 (*ortho*-phenyl) in the ^1H NMR spectrum (Fig. 4b) and $\delta = 74.6$ in the ^{13}C NMR spectrum. Leaving the mixture to stand at room temperature for 1 week resulted in a complete disappearance of the signals due to the two intermediates, **15a** and **16a** (Fig. 4c). These observations suggest that **15a** is a kinetic product, and that it isomerizes to **16a** at room temperature (Scheme 2).

The NMR data mentioned above were not sufficient to determine the structures of **15a** and **16a** unambiguously. Since we could not obtain single crystals of **15a** or **16a** suitable for X-ray crystallography in spite of much effort, we next examined the oxidation of 6-(1-adamantyl)-6-phenylpentathiane (**7**) with DMD. The oxidation proceeded in a course quite similar to that for **5** to give monoxide **15b** and **16b**, corresponding to **15a** and **16a**, respectively. In the ^{13}C NMR spectrum, the pentathiane carbons due to **15b** and **16b** were observed at $\delta = 90.5$ and 76.2 , respectively (Scheme 2). Single crystals of a

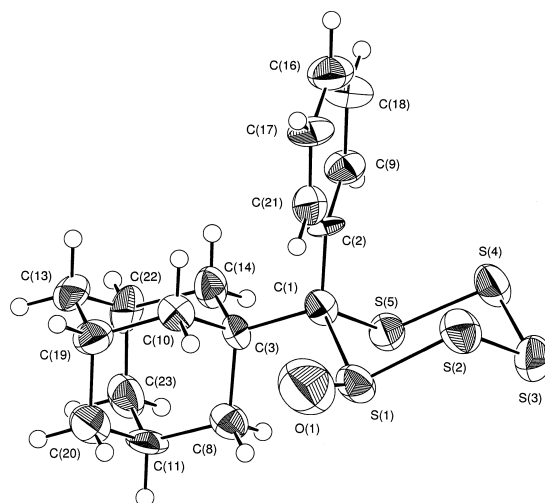
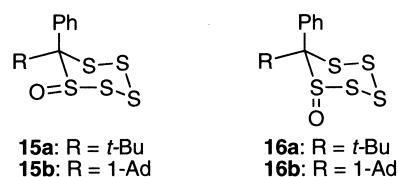


Fig. 5. Molecular structure of 6-(1-adamantyl)-6-phenylpentathiane 1-oxide (**15b**).



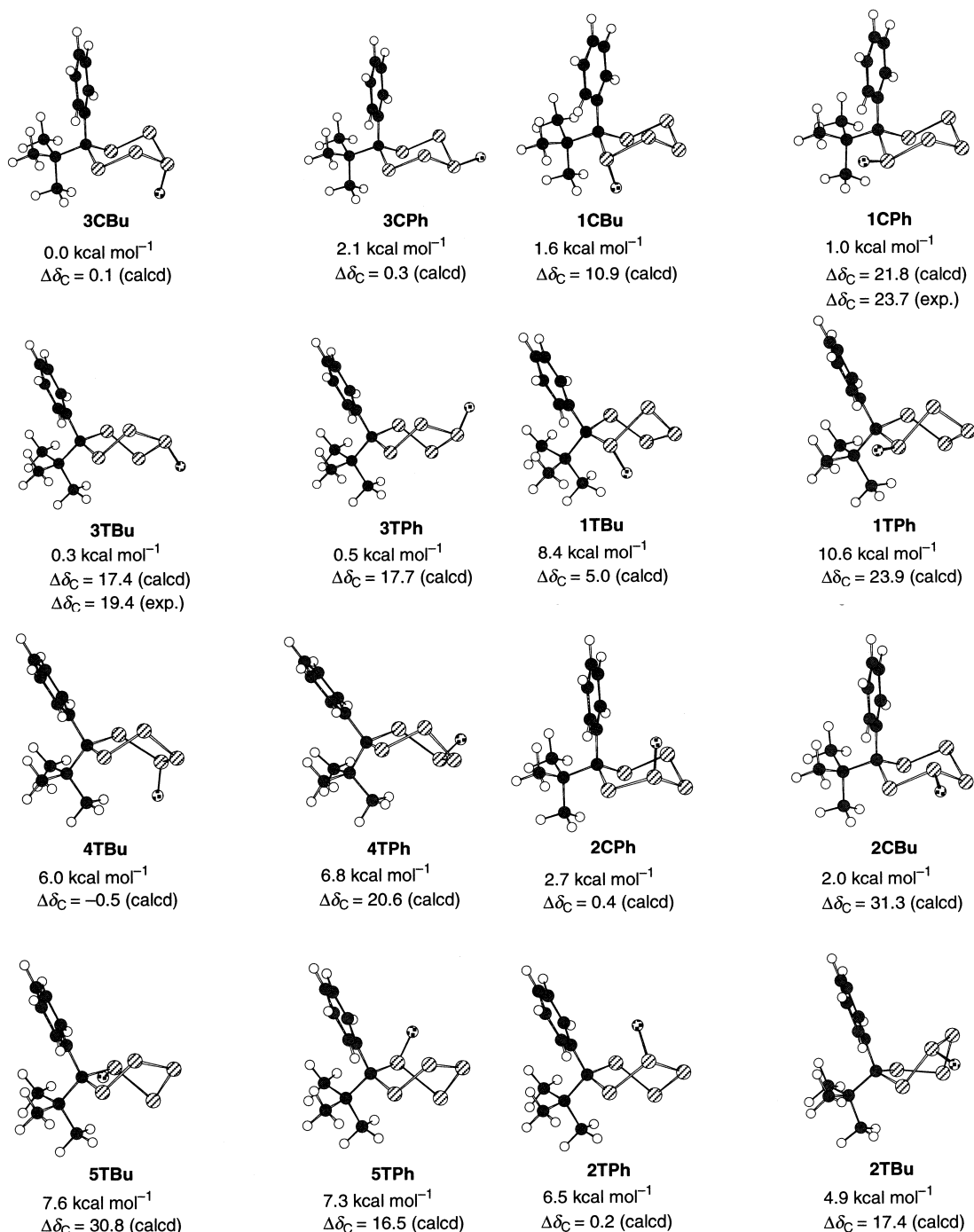


Fig. 6. ΔE (kcal mol^{-1}) and calculated down-field shifts [$\Delta\delta_{\text{C}} \text{ (calcd)} = 106.4 \text{ (chair-5)} - \sigma$] of pentathiane carbons. Experimental values [$\delta_{\text{C}} \text{ (exp.)}$] are also given.

kinetic product **15b** were obtained by repeating low-temperature recrystallization and, despite the low quality of the crystals, an X-ray crystallographic analysis exhibited undoubtedly that **15b** is a 1-oxide taking a chair conformation with the oxygen atom sharing an equatorial position (Fig. 5). We assigned the structure of **16** as the epimer of **15** (Chart 1) based on the NMR behavior mentioned above and DFT calculations of the NMR chemical shifts, as discussed later.

DFT Calculations. The energies (E) and NMR shielding constants (σ) by the GIAO method¹⁶ were calculated for all

possible regio- and stereoisomers of pentathiane monoxides and the two conformers of the starting pentathiane **5** at the B3LYP/6-31G* level.¹⁷ There are chair and twist conformations for each monoxide, and a monoxide has two epimers with respect to the S=O group. In addition, a twist 1-oxide (see **1TBu** in Fig. 6) and the corresponding twist 5-oxide (see **5TBu** in Fig. 6) are diastereomeric to each other because the twist conformation of pentathiane **5** has two enantiomeric forms. The same is true of the twist forms of the 2- and 3-oxides. Thus, calculations were performed on sixteen pen-

tathiane monoxides.

Relative Energies. Figure 6 summarizes the optimized structures and the relative energies (ΔE) of pentathiane monoxides, where we use abbreviations for convenience; for example, **1CBu** means that it is the 1-oxide taking a chair conformation with the oxygen atom cis to the *t*-Bu group, and **1TPh** means 1-oxide, a twist conformation, and the oxygen atom cis to the phenyl group. Figure 6 also includes the calculated down-field shifts ($\Delta\delta_c$) of pentathiane carbons relative to that of pentathiane **5**.

The most stable form of monoxides is **3CBu**, which is 0.3 kcal mol⁻¹ (1 cal = 4.184 J) more stable than **3TBu**, corresponding to the actual structure of the 3-oxide.⁸ The third monoxide in the energy level is **3TPh**, which is the epimer of **3TBu**. Another isolable isomer, **1CPh**, is the fourth in the energy level, and is more stable than the epimer **1CBu** by 0.5 kcal mol⁻¹. It is worth noting that the twist forms of the monoxides (*n*TR: *n* = 1,2,4,5; *R* = Bu, Ph), except for 3-oxides (**3TBu** and **3TPh**), are rather less stable than the most stable **3CBu** by from 4.9 (**2TBu**) to 10.6 (**1TPh**) kcal mol⁻¹. The results of calculations are approximately in harmony with the fact that **3TBu** and **1CPh** are isolable monoxides.

NMR Shielding Constants. Throughout this paper, pentathiane **5** is taken as the reference compound and the following criteria are adopted (see Figs. 7a and 7b). In the aliphatic region of the ¹H NMR spectra, the averaged value of calculated shielding constants (σ given with the ppm unit) of nine hydrogens of the *t*-butyl (σ = 31.17) is put at δ = 1.07, which is the experimental chemical shift of the *t*-butyl at 272 K. Similarly, in the aromatic region of the ¹H NMR spectra, the σ value of the *para*-hydrogen (σ = 24.91) is put at δ = 7.42, the experimental chemical shift of the corresponding proton at 272 K. Thus, calculated chemical shifts are given by the following equations: $\delta_H = (31.17 + 1.07) - \sigma$ for methyls and $\delta_H = (24.91 + 7.42) - \sigma$ for aromatic protons (Table 1).

First, we inspected the agreement of the calculations with the experimental values on the chair form of pentathiane **5** and the 3-oxide **6** (**3TBu**) to support the results of dynamic ¹H NMR spectroscopies.⁸ Figures 7a and 7b depict the experimental ¹H NMR spectrum (272 K) and the corresponding calculated one of pentathiane **5**, respectively. At 183 K in CD₂Cl₂ (Fig. 7c), three methyls of the *t*-butyl are divided into two singlets at δ = 0.87 and 1.47 in a ratio of 2:1. The calculated chemical shift difference between the two (δ_H = 0.88 and 1.45, Fig. 7d) is 0.57 ppm, which is very close to the experimental value of 0.60 ppm (Fig. 7). Meanwhile, the calculated chemical shifts of three methyls in the twist form of **5** are δ_H = 0.89, 0.95, and 1.65. Thus, the calculated spectra for the chair form (Figs. 7b and 7d) are in good agreement with the experimental spectra (Figs. 7a and 7c).

The calculated spectra for 3-oxide **6** also gave good agreement with the experimental ones. Figures 8a–c show an experimental spectrum of **6** at 285 K in CD₂Cl₂ and the corresponding calculated spectra of the two forms, **3TBu** and **3CBu**, respectively. At this temperature, the *t*-butyl and the phenyl groups rotate freely. On the other hand, Figs. 8e and 8f are the calculated spectra of **3TBu** and **3CBu**, respectively, which correspond to an experimental spectrum at 183 K (Fig. 8d), where the free rotation of the *t*-butyl and the phenyl groups is restrict-

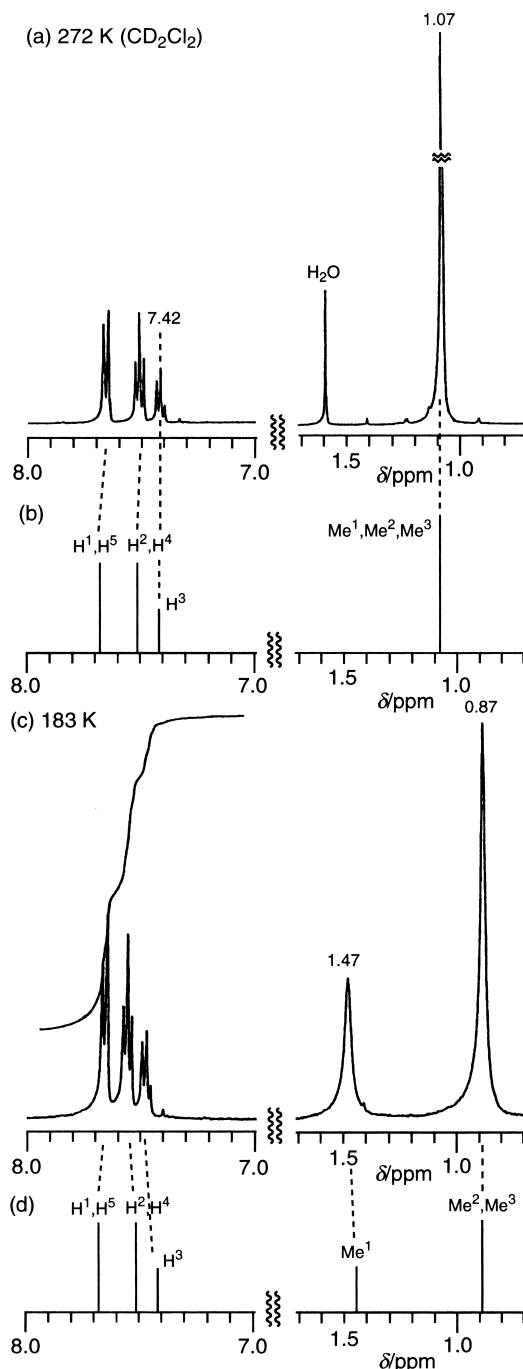
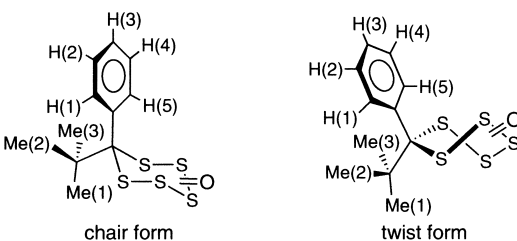


Fig. 7. Experimental and calculated NMR spectra of pentathiane **5**: (a) 272 K in CD₂Cl₂; (b) chair-**5**; (c) 183 K in CD₂Cl₂; (d) chair-**5**.

ed so that the three methyls of the *t*-butyls and the five phenyl protons are put independently. In both cases, the calculated spectra of **3TBu** are in much better agreement with the experimental spectra, particularly in the aromatic region, than those of **3CBu**. Some small unidentified signals appear in Figs. 8a and 8d. These signals (ticked by #) might be assigned to those due to **3CBu**. However, at present, we do not have any other evidence showing the existence of **3CBu**.

Another probe for elucidating the structures of pentathiane monoxides is by comparing the ¹³C NMR chemical shifts; spe-

Table 1. Calculated ^1H NMR Chemical Shifts (δ_{H}) of Pentathiane **5** and the Monoxides


Compounds	Me(1) ^{a)}	Me(2) ^{a)}	Me(3) ^{a)}	^t Bu ^{a)}	H(1) ^{b)}	H(2) ^{b)}	H(3) ^{b)}	H(4) ^{b)}	H(5) ^{b)}
5 (chair)	1.45	0.88	0.88	1.07	7.68	7.51	7.42	7.51	7.68
5 (twist)	1.65	0.95	0.89	1.16	7.71	7.38	7.36	7.32	7.23
1CBu	1.21	1.08	0.77	1.02	6.97	7.42	7.43	7.56	7.64
1CPh	1.43	1.24	0.96	1.21	8.42	7.55	7.47	7.46	7.29
1TBu	1.69	1.17	0.76	1.21	7.37	7.37	7.45	7.48	7.66
1TPh	1.38	1.00	0.89	1.09	8.79	7.50	7.51	7.39	7.51
2CBu	1.54	1.05	1.03	1.21	8.03	7.46	7.37	7.40	7.50
2CPh	1.35	0.96	0.95	1.08	8.08	7.42	7.38	7.41	7.67
2TBu	1.52	1.15	0.84	1.17	7.85	7.32	7.31	7.37	7.81
2TPh	1.45	1.11	1.00	1.18	8.05	7.27	7.27	7.25	7.19
3CBu	1.74	1.00	1.00	1.25	7.77	7.47	7.40	7.47	7.77
3CPh	1.55	0.95	0.95	1.15	7.82	7.61	7.51	7.61	7.82
3TBu	1.73	1.10	1.13	1.32	7.84	7.43	7.37	7.31	7.18
3TPh	1.47	0.99	1.20	1.22	7.89	7.48	7.44	7.42	7.59
4TBu	1.39	0.91	1.20	1.16	7.97	7.48	7.38	7.33	7.60
4TPh	1.14	0.78	1.25	1.06	8.02	7.49	7.44	7.41	7.75
5TBu	2.11	1.12	1.21	1.48	7.50	7.44	7.40	7.36	7.32
5TPh	1.82	0.95	0.88	1.22	7.64	7.40	7.41	7.36	7.46

a) $\delta_{\text{H}} = (31.17 + 1.07) - \sigma$. b) $\delta_{\text{H}} = (24.91 + 7.42) - \sigma$.

cifically, the chemical-shift difference between the pentathiane carbons of a monoxide and pentathiane **5** (Fig. 6). The calculated down-field shift ($\Delta\delta_{\text{C}}$) between chair-**5** and **3TBu** (twist-**6**), that is, σ 106.4 (chair-**5**) – σ 89.0 (**3TBu**), was 17.4 ppm, which is close to the experimental value of 19.4 ppm [δ 84.7 (**6**) – δ 65.3 (**5**)]. Similarly, the $\Delta\delta_{\text{C}}$ value for **15a** (**1CPh**) was 21.8 ppm; the deviation from the experimental value is only 1.9 ppm. The values of $\Delta\delta_{\text{C}}$ shown in Fig. 6 have a range from –0.5 ppm (**4TBu**) to 31.3 ppm (**2CBu**), indicating that the values are considerably sensitive to any structure change. Meanwhile, the shielding constant for tetramethylsilane carbon (TMS) at the same level was 189.7, giving the calculated chemical shift of the pentathiane carbon of **5** relative to TMS as $\delta = 83.3$.

For a further verification of the validity of the calculations for the ^{13}C NMR chemical shifts, we carried out calculations on 5,5-di-*t*-butyltetrathiolane 2-oxide **17**, 2,3-dioxide **18**, and the tetrathiolane **19** as a reference compound (Fig. 9). These compounds correspond to 1-adamantyl-*t*-butyl derivatives **2**, **3**, and **1** (Scheme 1).⁷ The tetrathiolane carbon of **3** ($\delta = 153.9$) is considerably deshielded, and this large down-field shift is satisfactorily reproduced. Thus, the calculated $\Delta\delta_{\text{C}}$ values would be valid within a few ppm in a range of 0–40 ppm for compounds of the same skeleton.

The results described above enable us to elucidate the structures of unisolable isomers of pentathiane monoxides by comparing the experimental ^1H and ^{13}C NMR data with the calculated NMR chemical shifts. The structure of 1-oxide **16a**, ap-

pearing in Fig. 4, was thus assigned to be **1CBu**. Figure 10 shows the calculated ^1H NMR spectra of a pair of epimers, **1CPh** (**15a**) and **1CBu** (**16a**), below the experimental spectrum of the reaction mixture. The calculations well reproduced the down- and up-field shifts of the H(1) protons of the phenyl groups of **15a** and **16a**, respectively, despite a relatively large deviation of H(1) in **15a**. In ^{13}C NMR spectroscopy, the calculated $\Delta\delta_{\text{C}}$ of the pentathiane carbon of **16a** was 10.9 ppm, which is in good agreement with the experimental value of 9.3 ppm [$\delta = 74.6(\text{exp.})$].

In Figs. 4a and 4b, clear but unassigned signals were observed at $\delta = 1.19$ (*t*-Bu) and 8.04 (d, $J = 7.3$ Hz, *o*-Ph). Monoxides **2CBu** and **2CPh** might be candidates from the viewpoint of the calculated chemical shifts (Table 1) and the relative stabilities shown in Fig. 6. In the ^{13}C NMR spectrum of the reaction mixture, however, we observed not the pentathiane carbon signal due to **2CBu** ($\Delta\delta_{\text{C}} = 31.3$ ppm) or **2CPh** ($\Delta\delta_{\text{C}} = 0.4$ ppm), but a small unknown signal at $\delta = 103.0$ ($\Delta\delta_{\text{C}} = 38.0$ ppm). We therefore cannot rule out the possibility that the signals are due to a higher oxide of pentathiane **5**.

Regioselectivity of Oxidation of Pentathiane 5. The oxidation of **5** with $\text{CF}_3\text{CO}_3\text{H}$ took place at the 3-position to give **6** in at least 58% yield; we did not observe the formation of 1-oxide, **15a** or **16a**, at all. Because 20% is the statistical percentage for one sulfur atom of the pentasulfide linkage of **5**, the oxidation with $\text{CF}_3\text{CO}_3\text{H}$ is meaningfully regioselective. Table 2 gives the charge distributions of pentathiane **5**, calcu-

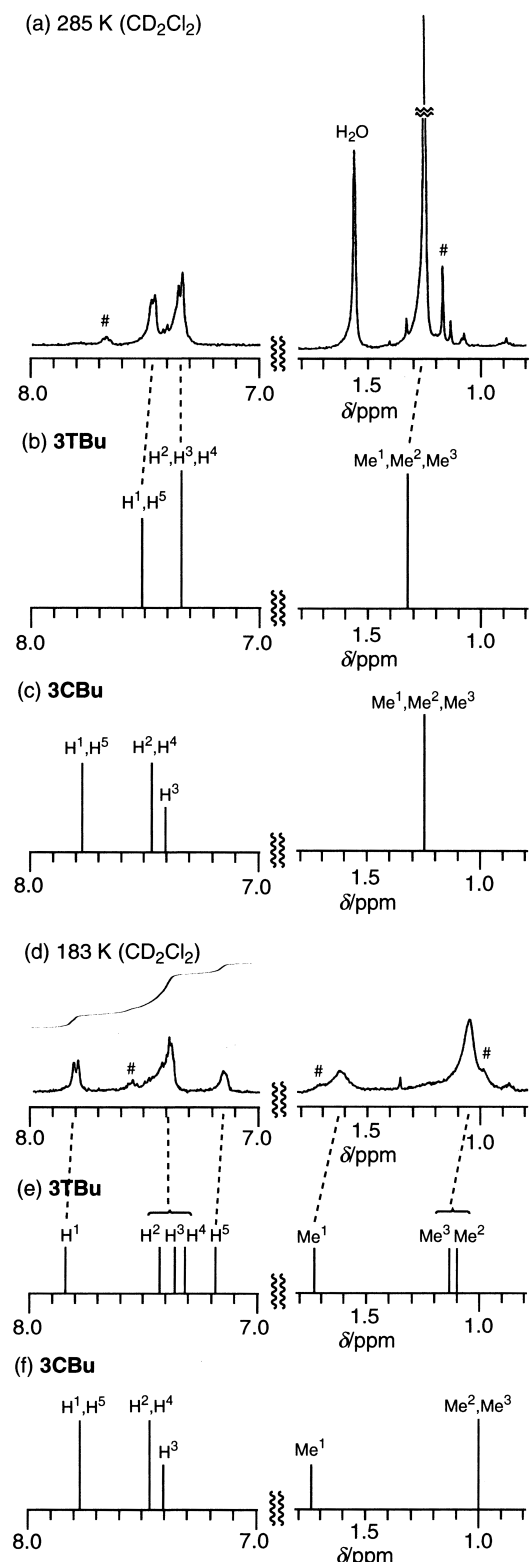


Fig. 8. Experimental and calculated ^1H NMR spectra of pentathiane 3-oxide **6**: (a) 285 K in CD_2Cl_2 , (b) **3TBu**, (c) **3CBu**, (d) 183 K in CD_2Cl_2 , (e) **3TBu**, (f) **3CBu**.

lated by the Mulliken population analysis, the natural population analysis (NPA),¹⁸ the Breneman CHelpG scheme,¹⁹ and the Merz–Kollman–Singh scheme (MK)²⁰ at the B3LYP/6-

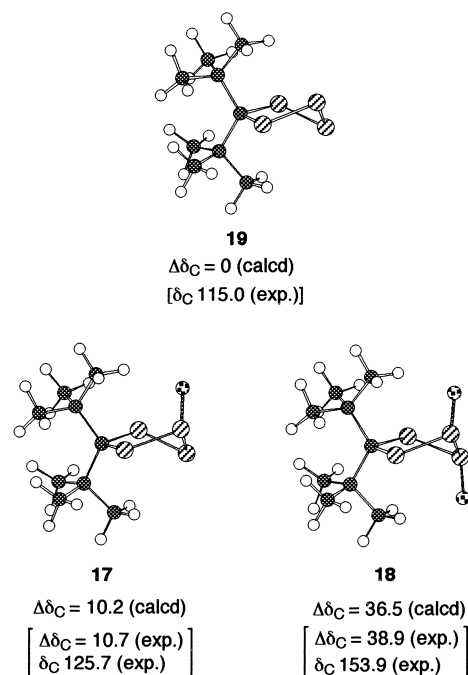


Fig. 9. Calculated $\Delta\delta_{\text{C}}$ values of tetrahydrothiophene carbons of 5,5-di-*t*-butyltetrahydrothiophene (**19**), the 2-oxide (**17**), and the 2,3-dioxide (**18**). Experimental values of 5-(1-adamantyl)-5-*t*-butyltetrahydrothiophene (**1**) and the oxides **2** and **3** are given in brackets.

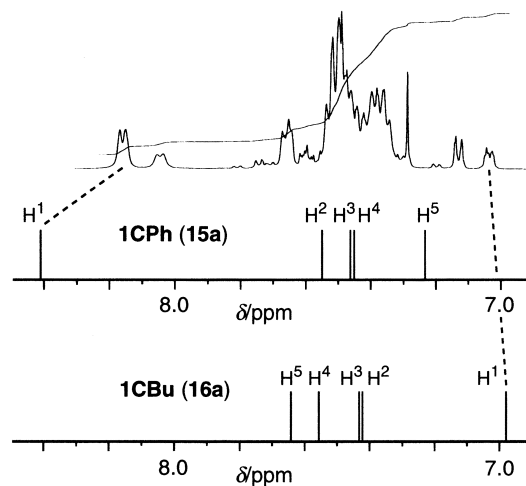


Fig. 10. Calculated ^1H NMR spectra of **15a** (**1CPh**) and **16a** (**1CBu**).

31G* and MP2/6-31G* levels. Except for the results of the CHelpG scheme, the charge distribution is the highest at the 3-position. Thus, the regioselectivity would be explained in terms that $\text{CF}_3\text{CO}_2\text{H}$ attacks the most electron-rich and sterically least hindered 3-position.

On the other hand, oxidation with DMD gave 1-oxide **15a**, mainly in 45% yield, and 3-oxide **6** in 9% yield. The oxidation in the presence of trifluoroacetic acid did not influence the results. The yields were roughly estimated from the ^1H NMR integral ratio of the reaction mixture, and we could not determine whether pentathiane 2-oxides were formed or not. Neverthe-

Table 2. Charge Distribution of Pentathiane 5

Methods	S-1 (S-5)	S-2 (S-4)	S-3	C-1
B3LYP/6-31G*				
Mulliken	0.034	-0.017	-0.021	-0.350
NPA	0.116	-0.005	-0.015	-0.291
CHelpG	-0.076	-0.020	0.008	-0.380
MKS	0.029	0.014	0.007	-1.189
MP2/6-31G*				
Mulliken	0.052	-0.007	-0.010	-0.373
NPA	0.134	0.004	-0.005	-0.335
CHelpG	-0.082	-0.013	0.011	-0.454
MKS	0.072	0.020	0.019	-1.522

less, oxidation with DMD is regarded to be much less regioselective than that with $\text{CF}_3\text{CO}_3\text{H}$, which might be ascribed to the high electrophilic reactivity of DMD.²¹

Conclusion

We determined the structures of oxidation products of pentathianes 5 and 7 by a combination of X-ray crystallography, experimental NMR spectroscopies, and calculations of the NMR chemical shifts. We verified that the calculations on oxides of cyclic polysulfides reproduced the experimental data within an acceptable error, even at a relatively inexpensive level. Therefore, the calculations would be important for sulfur chemistry in particular because it is not easy to measure the ³³S NMR spectra in the structure elucidation process.

Experimental

General: Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ¹H (400 MHz) and ¹³C NMR (100.6 MHz) spectra were determined on Bruker AM 400 and ARX400 spectrometers at 25 °C using CDCl_3 as the solvent, unless otherwise noted. 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.

An acetone solution of dimethyldioxirane (DMD) was prepared by a reported method,²² and its concentration was determined prior to use by oxidizing thioanisole to its sulfoxide with this solution.

Column chromatography was performed with silica gel; the eluent is given in parentheses. Gel permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-908 using chloroform as the eluent. High-pressure liquid chromatography (HPLC) was performed with a packed SiO_2 column, INERT-SIL PREP-SIL (10 mm i.d. 250 mm, GL Science INC.); the eluent is given in parentheses.

Computational Methods: All calculations were performed with Gaussian 98W running on the Windows® operating system. The structure optimization shown in Fig. 6 took approximately 2 days per monoxide at the B3LYP/6-31G* level with a 1.2 GHz processor, while the GIAO calculation shown in Table 1 took approximately 2 hours for each compound.

Preparation of Pentathiane 5. To a mixture of *t*-butyl phenyl thioketone (8a) (3.01 g, 16.9 mmol) and elemental sulfur (1.66 g, 51.8 mmol) was added 1,3-dimethyl-2,4-imidazolidinone (DMI) (10 mL) under argon. The suspension was stirred at room

temperature for 6 days in the dark. The mixture was diluted with ether and hexane, and the precipitates were collected by filtration and washed with hexane several times to give hexathiepane 9a (2.91 g, 51%). The filtrate was washed with water, dried over MgSO_4 , and evaporated to dryness. The residue was subjected to column chromatography (hexane) to give a mixture of pentathiane 5 and 9a and a mixture of 8a and 1,2,4-trithiolane 10a. The mixture of 5 and 9a was separated by HPLC (hexane) to give 5¹² (599 mg, 11%) and 9a¹² (200 mg, 3%). The mixture of 8a and 10a was subjected to GPC to give 10a (294 mg, 9%).

6-*t*-Butyl-6-phenylpentathiane (5). Crystal data: $\text{C}_{11}\text{H}_{14}\text{S}_5$, M_w 360.5, colorless prisms, $0.40 \times 0.28 \times 0.20 \text{ mm}^3$, orthorhombic, space group $P2_1nb$, $a = 12.363(3)$, $b = 16.838(4)$, $c = 6.607(1) \text{ Å}$, $V = 1375.3(5) \text{ Å}^3$, $\rho_{\text{calcd}} = 1.480 \text{ g cm}^{-3}$, $Z = 4$, $\mu(\text{Cu-K}\alpha) = 74.364 \text{ mm}^{-1}$. Mac Science MXC3KHF diffractometer with graphite-monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ Å}$), $\theta/2\theta$ scans method in the range $3^\circ < 2\theta < 140^\circ$ ($0 < h < 15$, $0 < k < 20$, $-8 < l < 0$), 1594 reflections measured, 1364 independent reflections. The structure was solved by direct methods using SIR92²³ in the CRYSTAN GM program system, and refined by a full-matrix least-squares method using all (1364) reflections for 191 parameters. An absorption correction was made by the psi-scan method. The non-hydrogen atoms were refined anisotropically. The final $R (R_w) = 0.0350$ (0.0470) and $\text{GOF} = 1.907$; max/min residual electron density = $0.23/-0.45 \text{ e Å}^{-3}$.

cis-3,5-Di-*t*-butyl-3,5-diphenyl-1,2,4-trithiolane (10a). Colorless crystals, mp 131–132 °C decomp (hexane/ CH_2Cl_2); ¹H NMR: δ 1.22 (s, 18H), 6.99–7.01 (m, 6H), 7.51–7.54 (m, 4H); ¹³C NMR: δ 28.8 (CH_3), 41.8 (C), 98.0 (C), 125.9 (CH), 126.4 (CH), 130.7 (CH), 140.9 (C); MS: m/z 388 (M^+). Found: C 68.30, H 7.31%. Calcd for $\text{C}_{22}\text{H}_{28}\text{S}_3$: C 67.99, H 7.26%. Crystal data for 10a: $\text{C}_{22}\text{H}_{28}\text{S}_3$, M_w 388.64, colorless prisms, $0.28 \times 0.28 \times 0.20 \text{ mm}^3$, monoclinic, space group $C2/c$, $a = 31.653(8)$, $b = 6.913(2)$, $c = 19.274(4) \text{ Å}$, $\beta = 96.25(2)^\circ$, $V = 4192(2) \text{ Å}^3$, $\rho_{\text{calcd}} = 1.231 \text{ g cm}^{-3}$, $Z = 8$, $\mu(\text{Cu-K}\alpha) = 31.722 \text{ mm}^{-1}$. Mac Science MXC3KHF diffractometer with graphite-monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ Å}$), $\theta/2\theta$ scans method in the range $3^\circ < 2\theta < 140^\circ$ ($0 < h < 38$, $-8 < k < 0$, $-23 < l < 23$), 4553 reflections measured, 3849 independent reflections. The structure was solved by direct methods using SIR92²³ in the CRYSTAN GM program system and refined by a full-matrix least-squares method using 3548 reflections [$I \geq 2\sigma(I)$] for 338 parameters. An absorption correction was made by the psi-scan method. The non-hydrogen atoms were refined anisotropically. The final $R (R_w) = 0.0787$ (0.0969) and $\text{GOF} = 2.748$; max/min residual electron density = $0.38/-0.94 \text{ e Å}^{-3}$.

Preparation of Pentathiane 7. To a mixture of 1-adamantyl phenyl thioketone (8b) (1.01 g, 3.94 mmol) and elemental sulfur (1.02 g, 31.8 mmol) was added DMI (5 mL) under argon. The suspension was stirred at room temperature for 4 days in the dark. The mixture was diluted with ether, and the precipitates were collected by filtration to give a mixture of pentathiane 7 and sulfur. The mixture was purified by column chromatography (hexane) to give 7¹² (1.13 g, 75%). The filtrate was washed with water, dried over MgSO_4 , and evaporated to dryness. The residue was purified by column chromatography (hexane), HPLC (hexane), and then recrystallization to give pentathiane 7 (63 mg, 4%), hexathiepane 9b⁸ (58 mg, 4%), and 1,2,4-trithiolane 10b (40 mg, 4%).

cis-3,5-Di(1-adamantyl)-3,5-diphenyl-1,2,4-trithiolane (10b). Colorless crystals, mp 217–218 °C decomp (hexane/ CH_2Cl_2); ¹H NMR: δ 1.54–1.62 (m, 12H), 1.82–2.01 (m, 12H),

1.98 (br s, 6H), 6.94–6.98 (m, 6H), 7.44–7.46 (m, 4H); ^{13}C NMR: δ 28.9, 36.5, 39.8, 43.0, 98.2, 125.7, 126.3, 131.2, 140.0; MS: m/z 544 (M^+); Found: C 74.67, H 7.39%. Calcd for $\text{C}_{34}\text{H}_{40}\text{S}_3$: C 74.94, H 7.40%.

Oxidation of Pentathiane 5 with $\text{CF}_3\text{CO}_3\text{H}$. (i) NMR observation. To a solution of pentathiane **5** (33.3 mg, 0.109 mmol) and 30% hydrogen peroxide (17 mg, 0.15 mmol) in CH_2Cl_2 (5 mL) was added trifluoroacetic anhydride (0.08 mL, 0.57 mmol) at -20°C under argon. After the mixture was stirred for 20 min at -20°C , volatile materials were removed in vacuo below -20°C . An ^1H NMR measurement of the residue showed the presence of 3-oxide **6** (41%), pentathiane **5** (30%), and thioketone *S*-oxide **11a**²⁴ (1%).

(ii) Isolation of 3-oxide **6**. To a solution of pentathiane **5** (77.5 mg, 0.253 mmol) and 30% hydrogen peroxide (61 mg, 0.52 mmol) in CH_2Cl_2 (6 mL) was added trifluoroacetic anhydride (0.11 mL, 0.79 mmol) at -20°C under argon. The mixture was stirred for 20 min at -20°C , and then diluted with aq. Na_2SO_3 . The mixture was neutralized with aq. NaHCO_3 and extracted with CH_2Cl_2 . The extract was washed with water, dried over MgSO_4 , and evaporated to dryness. The thus-obtained yellow oil was washed with hexane two times at -30°C , and a resulting yellow solid was recrystallized from a mixed solvent of hexane and CH_2Cl_2 to give 3-oxide **6** (20 mg, 25%).

***c*-6-*t*-Butyl-*t*-6-phenylpentathiane *r*-3-Oxide (**6**).** Yellow crystals, mp $95\text{--}96^\circ\text{C}$ decomp (hexane/ CH_2Cl_2); ^1H NMR (283 K): δ 1.25 (s, 9H), 7.30–7.38 (m, 3H), 7.42–7.50 (m, 2H); ^{13}C NMR (283 K): δ 27.0, 43.6, 84.7, 127.6, 128.1, 130.9, 136.8; IR (KBr): 1094 cm^{-1} (S=O). Found: C 40.08, H 4.31%. Calcd for $\text{C}_{11}\text{H}_{14}\text{OS}_5$: C 40.96, H, 4.37% (contamination with a small amount of elemental sulfur caused the unsatisfactory result). Crystal data for **6**: $\text{C}_{11}\text{H}_{14}\text{OS}_5$, M_w 332.53, yellow plates, $0.30 \times 0.16 \times 0.06 \text{ mm}^3$, monoclinic, space group $P2_1/c$, $a = 10.290(1)$, $b = 20.718(2)$, $c = 6.6140(5) \text{ \AA}$, $\beta = 93.555(4)^\circ$, $V = 1407.3(2) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.522 \text{ g cm}^{-3}$, $F(000) = 672$, $\mu(\text{Mo-K}\alpha) = 0.80 \text{ mm}^{-1}$. Mac Science DIP3000 diffractometer with a graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data reduction was made by the maXus program system. Intensity data of 2871 unique reflections were collected in the range of $0 \leq h \leq 13$, $-26 \leq k \leq 0$, $-0 \leq l \leq 7$. 1915 reflections [$I \geq 2\sigma(I)$] were used for refinement (210 parameters). The final $R_1 = 0.049$, $wR_2 = 0.064$, and GOF = 1.585; max/min residual electron density = $0.72/-0.38 \text{ e \AA}^{-3}$.

Oxidation of Pentathiane 5 with DMD. (i) Determination of final products. To a solution of **5** (25.2 mg, 0.0822 mmol) in CH_2Cl_2 (5 mL) was added an equimolar amount of DMD (0.10 M, 0.81 mL, 0.081 mmol) (1 M = 1 mol dm^{-3}) at -20°C under argon. The mixture was stirred for 2 h at -20°C and volatile materials were removed in vacuo below -20°C . The residue was dissolved in CH_2Cl_2 (5 mL) and the solution was stirred for 3 h at room temperature. The yields of products were calculated based on the integral ratio of the ^1H NMR spectrum of the mixture as follows: dithiirane 1-oxide **12**,¹¹ 25%; **11a**, 17%; **11b**, 9%; **5**, 13%, **9a**, 8%; **13**, 12%; **6**, 9%; **10a**, 1%.

(ii) NMR observation. To a solution of **5** (40 mg, 0.13 mmol) in CH_2Cl_2 (6 mL) was added 1.5 molar amounts of DMD (0.083 M, 2.4 mL, 0.20 mmol) at -20°C under argon. The mixture was stirred for 1.5 h at -20°C and volatile materials were removed in vacuo below -20°C . The residue was dissolved in CDCl_3 and subjected to NMR measurements (see Fig. 4). The final ratio of **12**:**11a**:**11b**:**5**:**9a**:**13**:**6** was 20:21:18:7:10:9:8.

Oxidation of Pentathiane 7 with DMD. To a solution of

pentathiane **7** (162 mg, 0.422 mmol) in CH_2Cl_2 (50 mL) and C_6H_6 (10 mL) was added DMD (0.088 M, 5.7 mL, 0.50 mmol) at -20°C under argon. The mixture was stirred for 1 h at -20°C and volatile materials were removed in vacuo below -20°C . The residue was washed with hexane two times and recrystallized from a mixed solvent of hexane and CH_2Cl_2 three times to give crude **15b** (96 mg, 57%) contaminated with **7**: Mp $78\text{--}81^\circ\text{C}$ decomp. Single crystals subjected to X-ray crystallography were obtained by further recrystallization.

***t*-6-(1-Adamantyl)-*c*-6-phenylpentathiane *r*-1-Oxide (**15b**):** Crystal data: $\text{C}_{17}\text{H}_{20}\text{OS}_5$, M_w 400.67, yellow plates, $0.20 \times 0.14 \times 0.04 \text{ mm}^3$, space group monoclinic, $P2_1/c$, $a = 18.537(4)$, $b = 6.765(1)$, $c = 23.372(4) \text{ \AA}$, $\beta = 144.06(1)^\circ$, $V = 1720.3(6) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.547 \text{ g cm}^{-3}$, $F(000) = 840$, $\mu(\text{Mo-K}\alpha) = 0.67 \text{ mm}^{-1}$. Mac Science DIP3000 diffractometer with a graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data reduction was made by the maXus program system. Intensity data of 3358 unique reflections were collected in the range of $-23 \leq h \leq 0$, $-8 \leq k \leq 0$, $-17 \leq l \leq 29$. 2329 reflections [$I \geq 0.5\sigma(I)$] were used for refinement (208 parameters). Nonhydrogen atoms were refined anisotropically and hydrogen atoms were placed at calculated positions. The final $R_1 = 0.159$ (0.213 for all), $wR_2 = 0.108$, and GOF = 2.263; max/min residual electron density = $1.17/-0.88 \text{ e \AA}^{-3}$. Although the R values were not satisfactorily low, the peak height of the oxygen atom (415) was high enough compared with those of carbon atoms (423–289). We therefore rule out a possibility that the present structure was one of plural regio- and stereoisomers forming mixed crystals. Selected bond lengths ($\text{\AA}$) and angles (deg.) under such circumstances for tentative information: C1–S1, 1.90(2); S1–S2, 2.133(7); S2–S3, 2.015(8); S3–S4, 2.024(8); S4–S5, 2.025(7); S5–C1, 1.86(2); C1–C2, 1.48(2); C1–C3, 1.57(2); S1–O1, 1.41(2); S2–S1–C1, 101.4(6); S1–S2–S3, 98.9(3); S2–S3–S4, 100.9(4); S2–S1–O1, 103.5(7); O1–S1–C1, 111.8(9); S3–S4–S5, 103.0(3); S4–S5–C1, 105.5(6); S1–C1–S5, 99.8(8); C2–C1–C3, 113.3(14).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-165141 (**5**), CCDC-165142 (**10a**), CCDC-165143 (**6**), and CCDC-165144 (**15b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk). The details of structures have been deposited as Document No. 75006 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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