

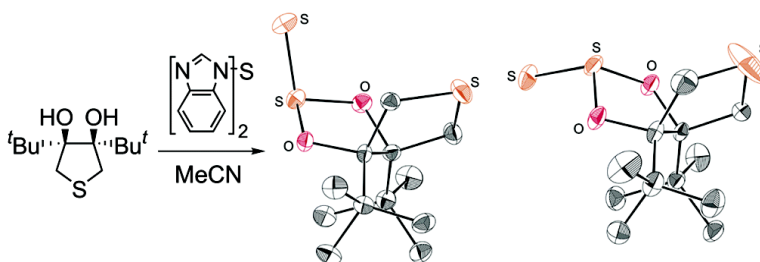
Communication

The Thiosulfinyl Group Serves as a Stereogenic Center and Shows Diamagnetic Anisotropy Similar to That of the Sulfinyl Group

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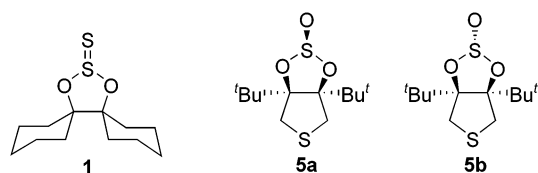
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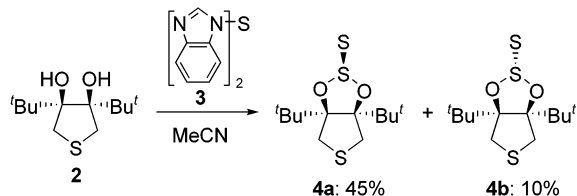
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The chemistry of compounds having the general structure of $R_2S=S$ has attracted much attention because of the expected intriguing properties of the thiosulfinyl group.¹ Although thio-sulfoxides ($R = \text{alkyl or aryl for } R_2S=S$) have long been proposed as transient intermediates, they still elude even detection by spectroscopies.¹ On the other hand, thionosulfites $[(RO)_2S=S]$ are more stable than thio-sulfoxides because of electronic stabilization by the oxygen atoms.^{2,3} Thus, Harpp et al. succeeded in the synthesis and X-ray single-crystal structure analysis of the thionosulfite **1**.^{3a} Here, we report the synthesis, X-ray crystallographic analysis, and chemical and spectroscopic properties of a pair of isolable, diastereomeric thionosulfites **4a** and **4b**.

Initially, we obtained sulfite **5** as a mixture of diastereomers **5a** and **5b**,⁴ as the precursor to **4**, by condensation of *cis*-3,4-di-*tert*-butylthiolane-3,4-diol (**2**)⁵ with $SOCl_2$.⁶ Disappointingly, however, attempted conversion of **5** to **4** by treatment with Lawesson's reagent was unsuccessful. We then applied the Harpp method to obtain **4** from **2** directly.^{3a} Thus, **2** was treated with 4 molar amounts of 1,1'-thiobisbenzimidazole (**3**)⁷ in MeCN for 72 h at room temperature. The expected reaction took place to give a diastereomeric mixture of thionosulfites **4a** and **4b** in the ratio 82:18 (Scheme 1). Separation of the diastereomers could be satisfactorily performed by HPLC to afford **4a** and **4b** in 45% and 10% isolated yields, respectively.⁸



Scheme 1. Synthesis of **4a** and **4b**



The stereochemistry of **4a** and **4b** was established by X-ray crystallographic analyses. Molecular structures of **4a** and **4b** are shown in Figure 1. Figure 2 shows the bond angles and bond lengths around the S=S group of **4a** and the S=O group of **5a**.⁶ The sum of the two O-S-S bond angles and the one O-S-O bond angle of **4a** is 311.5° and comparable to that of **5a** (309.5°), while it is smaller than the sum of the three H-C-H bond angles of methane (328.5°). Thus, the pseudotetrahedral geometry of the thiosulfinyl sulfur atom of **4a** is deeper than that of methane. Incidentally, the sum of the corresponding angles for **4b** is 310.4°. The S=S bond lengths of **4a** and **4b** are 1.9154(6) and 1.8964(13) Å, respectively,

and are comparable with that of **1** (1.901(2) Å). The two *tert*-butyl groups of **4a** and **4b** are twisted with dihedral angles of 43.7(2)° and 38.0(3)°, respectively, to reduce the steric repulsion. The optimized molecular structures of **4a** and **4b** (Figure 3), predicted by density functional theory (DFT) calculations (B3LYP/6-31G* level), are in good agreement with the experimental structures.⁹

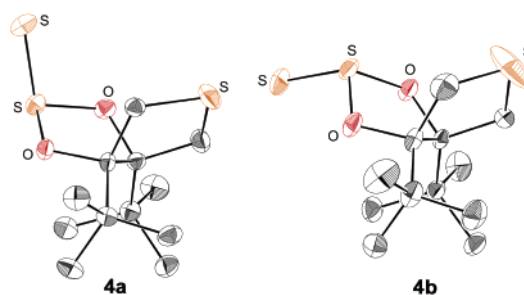


Figure 1. Molecular structures of **4a** and **4b**.

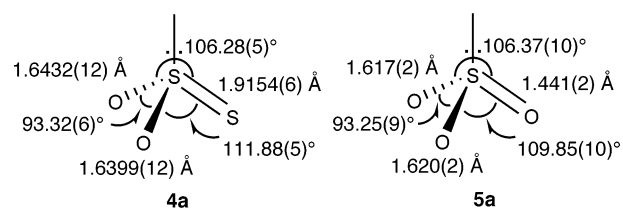


Figure 2. Bond angles and bond lengths around the S=S group of **4a** and the S=O group of **5a**.

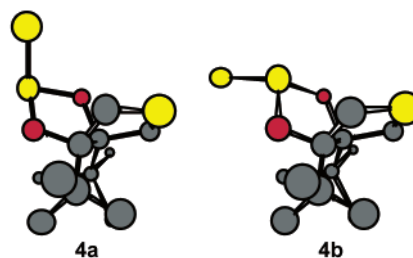
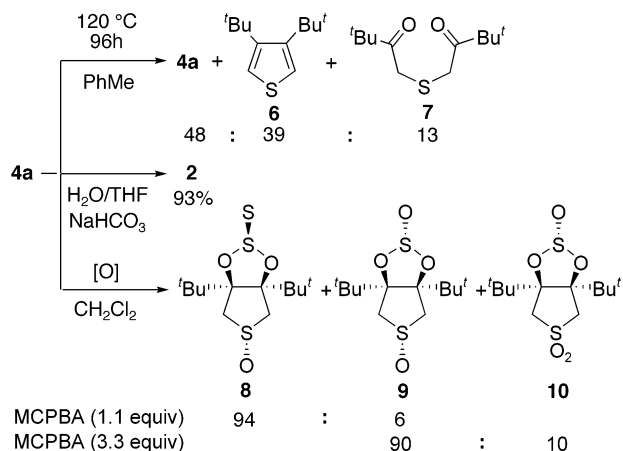


Figure 3. Optimized structures of **4a** and **4b**.

No thermal isomerization was observed between **4a** and **4b**, even when each isomer was heated at 120 °C in toluene- d_8 , indicating that the pseudotetrahedral geometry around the thiosulfinyl group is rigid enough to serve as a stereogenic center.¹⁰ However, decomposition of **4** took place instead; **4a** gave **6**, **7**,⁵ and **8** in the ratio 39:13:48 after heating for 96 h, while **4b** decomposed completely to produce **6** and **7** in the ratio 6:94 after heating for 24 h (Scheme 2). The experimental ratio of **4a** and **4b**, 82:18, is therefore kinetically controlled. The DFT calculations predicted that **4a** is more stable than **4b** by 1.69 kcal/mol. **4a** and **4b** are susceptible to alkaline hydrolysis. Thus, **4a** was hydrolyzed to give the diol **2** in 93% yield in the presence of $NaHCO_3$ in a 1:1 mixture

of H₂O and THF, whereas it remained unchanged in the absence of NaHCO₃ for several days. Oxidation of **4a** with 1.1 molar amounts of MCPBA gave **8** and **9** in the ratio 94:6 (**8** was isolated in 77% yield), while oxidation with 3.3 molar amounts of MCPBA furnished **9** and **10** in the ratio 90:10. The structure of **8** was determined by X-ray crystallographic analysis, while **9** and **10** agreed with the authentic samples prepared by oxidation of **5b**.⁶ These results reveal that the S=S group is more resistant toward oxidation than the sulfide sulfur atom, and interestingly the S=S group is converted to the S=O group with inversion of the configuration.

Scheme 2. Reactions of **4a**



As to the diamagnetic anisotropy of the S=S group, no data information has been available. Figure 4 shows the chemical shift data of the methylene protons of **4a** and **4b** and those of **5a** and **5b**; each methylene proton appeared as a doublet with $J = 13\text{--}14$ Hz due to geminal coupling.⁶ The assignments were based on NOE experiments. The inspection of these data reveals that the shielding and deshielding zones of the S=S group are similar to those of the S=O group. Therefore, the shielding and deshielding zones of the S=S group are assigned as depicted in Figure 5 by analogy of the well-documented corresponding zones of the S=O group.¹¹

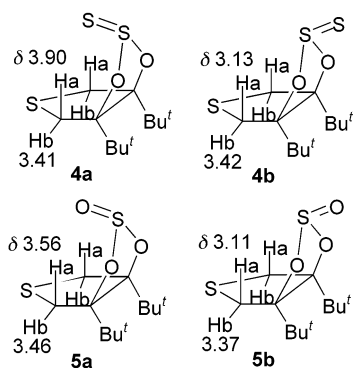


Figure 4. Chemical shift data of **4a,b** and **5a,b**.

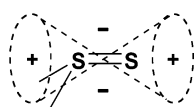


Figure 5. Shielding (+) and deshielding (-) zones of the S=S group.

The strong infrared absorption and Raman bands were observed for **4a** at 653 and 650 cm⁻¹, respectively. The DFT calculations of **4a** predicted the appearance of the strong infrared absorption band

and the medium-sized Raman band mainly due to the contribution of the S=S stretching vibration at 639 cm⁻¹. Therefore, these strong infrared and Raman bands at about 650 cm⁻¹ can be assigned to the S=S stretching vibration. Similarly, the strong Raman band assignable to the S=S stretching vibration was observed at 666 cm⁻¹ for **4b**. The corresponding infrared absorption band was observed at 665 cm⁻¹ as a shoulder of the strong 670 cm⁻¹ band. The DFT calculations of **4b** predicted the medium-sized infrared absorption band and the strong Raman band at 647 cm⁻¹, which are assigned to the S=S stretching vibration. The observed S=S stretching infrared and Raman bands at about 650 cm⁻¹ for **4a** and at about 666 cm⁻¹ for **4b** are in good agreement with the observed infrared and Raman bands for **1** at about 650 cm⁻¹.^{3b} The UV/vis spectrum of **4a** showed the two absorption maxima at 253 ($\epsilon = 2790$) and 324 (142) nm, while the time-dependent DFT calculations predicted the appearance of two strong absorptions at 249 and 263 nm and a weak absorption at 361 nm. Similarly, **4b** showed the two absorption maxima at 245 ($\epsilon = 3060$) and 313 (203) nm, although the calculation predicted the appearance of the two strong absorptions at 241 and 262 nm and the weak absorption at 351 nm. Also for **1**, the strong absorption at 250 nm and the weak absorption at 311 nm were reported.^{3b}

Supporting Information Available: Procedures for the preparation of **4** and other reactions, plausible mechanisms of the formation of **4** and other reactions, X-ray crystallographic data of **4a**, **4b**, and **8**, and calculated structural and spectral data of **4a** and **4b** (PDF, CIF, TIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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