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Sulfur-Substituted Tetrahedranes

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Supporting Information

ABSTRACT: The stable sulfur-substituted tetrahedrane derivatives **2**−**4** were synthesized by the reaction of tris(trimethylsilyl)tetrahedranyllithium **1** with diphenyl disulfide, bis(4-nitrophenyl) disulfide, and bis(2,4-dinitrophenyl) disulfide, respectively, and characterized by both NMR spectroscopy and X-ray crystallography. Phenylsulfonyltetrahedrane **5** was prepared by the reaction of **2** and *m*-chloroperbenzoic acid. The UV−vis absorption spectra of **2**−**4** suggested an interaction of the σ orbital of the tetrahedrane core and the lone-pair electrons on the sulfur atom, whereas no interaction for **5** was found. Thermal reactions of **2** and **5** are also reported; **2** underwent fragmentation into two acetylene molecules, whereas **5** gave the corresponding cyclobutadiene.

Tetrahedrane, cubane, and prismane are highly strained organic molecules.[1] Cubane and prismane were synthesized by Eaton and Cole[2] and Katz and Acton,[3] respectively, but all attempts to prepare the parent tetrahedrane have been unsuccessful because of its high strain energy.[1,4] In 1978, Maier and co-workers succeeded in synthesizing tetrakis(*tert*-butyl)tetrahedrane (^{t}Bu$_4$THD)[5] by photochemical isomerization of the corresponding cyclobutadiene (^{t}Bu$_4$CBD). In a similar manner, Maier and we succeeded in synthesizing tetrakis(trimethylsilyl)tetrahedrane [(Me$_3$Si)$_4$THD][6,7a] by photochemical isomerization of the corresponding cyclobutadiene ((Me$_3$Si)$_4$CBD).[7,8] The four σ-donating trimethylsilyl groups enhance the thermal stability of (Me$_3$Si)$_4$THD,[6,9] which is stable up to 300 °C. Furthermore, we demonstrated that (Me$_3$Si)$_4$THD could be transformed into tris(trimethylsilyl)tetrahedranyllithium **1** by reaction with methyllithium.[10] Since then, we have succeeded in introducing a smaller group (e.g., H or Me) to the tetrahedrane skeleton by reacting **1** with a variety of electrophiles.[10] Recently, we also reported the synthesis of perfluoroaryltetrahedranes, which exhibit $\sigma-\pi$ conjugation between the strained tetrahedrane core and the aromatic ring.[11] Introduction of a heteroatom such as N, O, S, or a halogen to the tetrahedrane core would be interesting because the tetrahedrane σ framework has the potential to interact with the nonbonding orbitals on the heteroatom; however, such heteroatom-substituted tetrahedrane derivatives have remained elusive because of the synthetic difficulty in preparing such molecules. Herein we report the synthesis of the first stable sulfur-substituted tetrahedrane derivatives **2**−**5**, which were characterized by NMR spectroscopy and X-ray diffraction. Evidence for the interaction of the σ orbital of the tetrahedrane core and the lone-pair electrons on the sulfur atom is also reported in this paper along with the unique thermal reactions.

A 1.5-fold excess of diphenyl disulfide was added at room temperature to a dark-brown solution of **1** in toluene. The reaction occurred gradually, and the color of the reaction mixture turned to pale-yellow. Tetrahedrane **2** was isolated by HPLC as a colorless oil in 55% yield (Scheme 1).[12] The introduction of 4-nitrophenylsulfanyl or 2,4-dinitrophenylsulfanyl groups into the tetrahedrane core was also possible and allowed us to obtain single crystals to perform crystallographic analyses (see below). Thus, **1** was treated with bis(4-nitrophenyl) disulfide in THF to give 4-nitrophenyl tetrahedranyl sulfide **3** as air-stable yellow crystals in 52% isolated yield. Similarly, **4** was obtained by the reaction of **1** with bis(2,4-dinitrophenyl) disulfide in THF, which gave **4** as air-stable orange crystals in 30% yield. Interestingly, we were able to oxidize the sulfide to the corresponding sulfone without any oxidation of the tetrahedrane core or the Si−C bonds in **2**. Thus, treatment of **2** with *m*-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 gave air-stable colorless crystals of phenylsulfonyltetrahedrane **5**, which was isolated in 90% yield (Scheme 2).[12]

The ^{13}C NMR signals of the tetrahedrane skeleton were observed at 3.9 ppm (C−SC$_6$H$_5$) and −15.0 ppm (C−SiMe$_3$) for **2**, 2.2 ppm (C−SC$_6$H$_4$NO$_2$) and −15.1 ppm (C−SiMe$_3$) for **3**, 2.2 ppm (C−SC$_6$H$_3$(NO$_2$)$_2$) and −14.5 ppm (C−SiMe$_3$) for **4**, and 16.4 ppm (C−S(O)$_2$C$_6$H$_5$) and −10.7 ppm (C−SiMe$_3$) for **5**. Although an upfield shift of the skeletal C atoms is typical for tetrahedranes, significant downfield shifts relative to (Me$_3$Si)$_4$THD (−20.5 ppm)[6] and **1** [−27.0 ppm (ring C−Li) and −22.0 ppm (ring C)][10] were observed for the sulfur-substituted carbon atom: +24.4 ppm for **2**, +22.7 ppm for **3**, +22.7 ppm for **4** and +36.9 ppm for **5** relative to (Me$_3$Si)$_4$THD. This remarkable deshielding could be attributed to the significant electron-withdrawing effect of the phenylsulfanyl and phenylsulfonyl groups on the tetrahedrane skeleton.

The molecular structure of **3**, as determined by X-ray crystallographic analysis, is shown in Figure 1.[12] The C1(tetrahedrane skeleton)−S1 bond length is 1.7167(13) Å, which is significantly shorter than the length of a typical C(sp^3)−S single bond (1.82 Å).[13] This shortening is attributed to the high s character of the carbon atom of the tetrahedrane core.[1] As a consequence of the difference in the electronegativities of the elements (Pauling electronegativities: Si, 1.90; S, 2.58),[14] the tetrahedrane skeleton in **3** is not symmetrical. Thus, the C(SC$_6$H$_4$NO$_2$)−C(SiMe$_3$) bond lengths (C1−C2, C1−C3, C1−C4) in **3** range from 1.4792(19) to 1.4876(18) Å (av 1.482 Å), whereas the C(SiMe$_3$)−C(SiMe$_3$) bond lengths (C2−C3, C2−C4 and C3−C4) range from 1.5041(19) to 1.5410(19) Å (av 1.518 Å). The C−C bond distances of the tetrahedrane core are similar to those previously observed for tetrahedrane derivatives with electron-withdrawing

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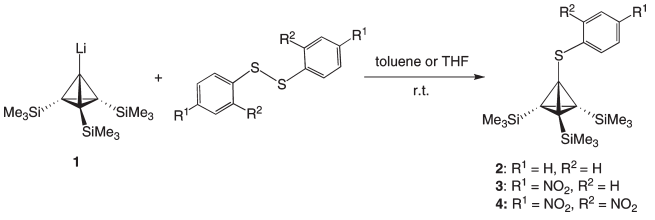
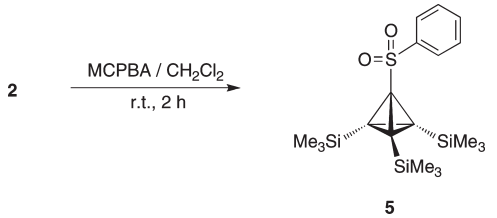
Scheme 1. Syntheses of Sulfur-Substituted Tetrahedranes 2, 3, and 4 by the Reaction of Tetrahedranyllithium 1 with the Corresponding Disulfides



Scheme 2. Synthesis of Sulfonyl-Substituted Tetrahedrane 5 by the Reaction of 2 with *m*-Chloroperbenzoic Acid



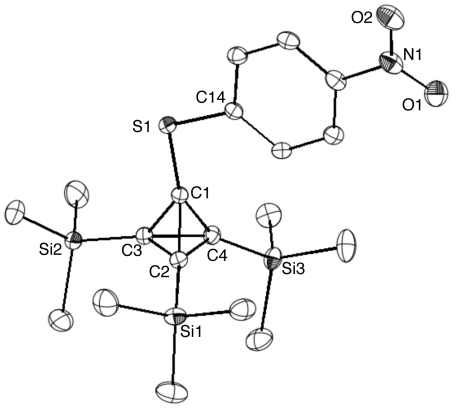


Figure 1. ORTEP drawing of **3** (30% thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C2, 1.4792(19); C1−C3, 1.4876(18); C1−C4, 1.4794(18); C2−C3, 1.5041(18); C3−C4, 1.5103(19); C4−C2, 1.5410(19); S1−C1, 1.7167(13); S1−C14, 1.7591(14); C2−Si1, 1.8293(15); C3−Si2, 1.8301(14); C4−Si3, 1.8362(14). C2−C1−C4, 62.78(9); C3−C1−C4, 61.20(9); C4−C1−C2, 62.78(9); C1−C2−C3, 59.81(9); C1−C2−C4, 58.61(9); C1−C3−C4, 59.13(9); C1−C3−C2, 59.26(9); C1−C4−C2, 58.60(9); C1−C4−C3, 59.67(9); C2−C3−C4, 61.49(9); C3−C4−C2, 59.06(9); C4−C2−C3, 59.45(9); C1−S1−C14, 102.91(7).

groups, such as perfluorophenyltetrahedrane, in which the C(C_6F_5)−C($SiMe_3$) bond lengths range from 1.475(2) to 1.504(2) Å (av 1.485 Å) and the C($SiMe_3$)−C($SiMe_3$) bond lengths range from 1.504(2) to 1.524(2) Å (av 1.512 Å).[11]

We also carried out X-ray analyses of **4** (see the Supporting Information) and **5** (Figure 2) and found that their tetrahedrane core structures are quite similar to that of **3**. The C1(tetrahedrane skeleton)−S1 bond length in **4** is 1.727(3) Å. In contrast, the C1(tetrahedrane skeleton)−S1 bond length in **5** is 1.6973(14). This result shows that the C(tetrahedrane skeleton)−S bond

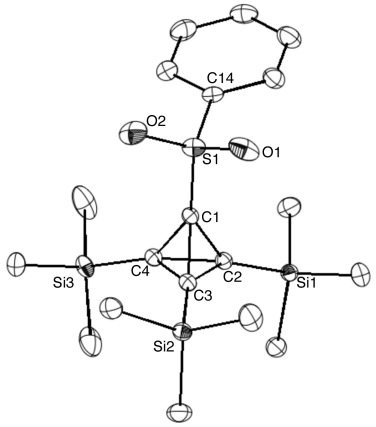


Figure 2. ORTEP drawing of **5** (30% thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C1−C2, 1.4792(19); C1−C3, 1.4932(19); C1−C4, 1.4739(19); C2−C3, 1.5022(18); C3−C4, 1.5111(19); C4−C2, 1.5276(19); S1−C1, 1.6973(14); S1−C14, 1.7650(15); C2−Si1, 1.8462(15); C3−Si2, 1.8361(14); C4−Si3, 1.8409(15). C2−C1−C3, 60.71(9); C3−C1−C4, 61.23(9); C4−C1−C2, 62.30(9); C1−C2−C3, 60.11(9); C1−C2−C4, 58.68(9); C1−C3−C4, 58.75(9); C1−C3−C2, 59.18(9); C1−C4−C2, 59.02(9); C1−C4−C3, 60.02(9); C2−C3−C4, 60.92(9); C3−C4−C2, 59.25(9); C4−C2−C3, 59.83(9); C1−S1−C14, 103.91(7).

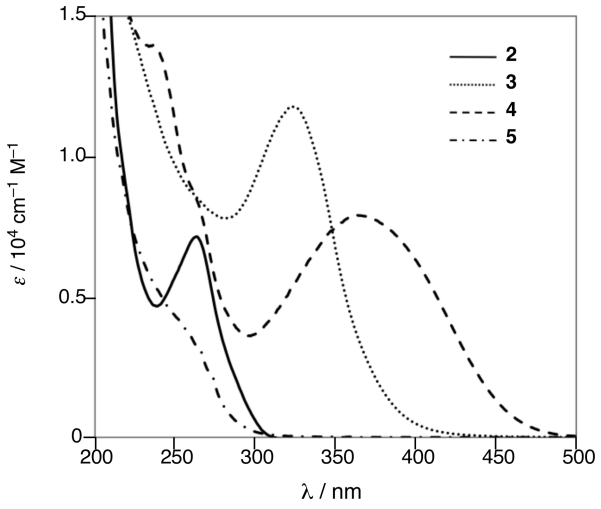


Figure 3. UV−vis spectra of **2**, **3**, **4**, and **5** in hexane.

length in sulfone **5** [1.6973(14) Å] is shorter than those in sulfides **3** and **4** [1.7167(13) Å and 1.727(3) Å, respectively], as is typical for sulfides and sulfones.[13]

The extended $\sigma-\pi$ conjugation in **2**−**4** is reflected in their electronic spectra. The absorption maxima in the UV−vis spectra of **2**, **3**, and **4** in hexane were observed at 273 nm (ε = 7300 cm^{-1} M^{-1}) for **2**, 324 nm (ε = 11 800 cm^{-1} M^{-1}) for **3**, and 362 nm (ε = 7900 cm^{-1} M^{-1}) for **4** (Figure 3). The bathochromic shifts of **3** and **4** in comparison with **2** are attributed to the influence of the nitro group on the phenyl ring, which lowers the π^* level of the phenyl group. However, the absorption maximum in the UV−vis spectrum of **5** in hexane was not observed in these regions, indicating a larger HOMO−LUMO gap than those in sulfides **2**, **3**, and **4**. This is probably due to the lack of conjugation between the tetrahedrane σ unit and the phenylsulfonyl group in **5**. The HOMOs

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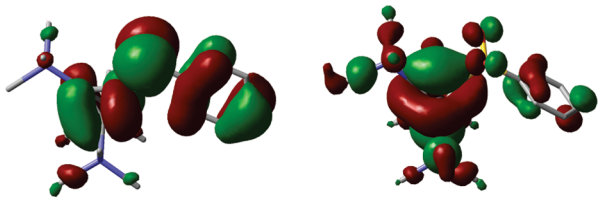


Figure 4. HOMOs of (left) **2** and (right) **5** calculated at the B3LYP/6-31G(d) level.

Scheme 3. Thermal Reaction of 2 To Give Bis(trimethylsilyl)-acetylene (6) and Phenyl Trimethylsilylethynyl Sulfide (7) and Thermal Reaction of 5 To Form (Phenylsulfonyl)tris(trimethylsilyl)cyclobutadiene (8)

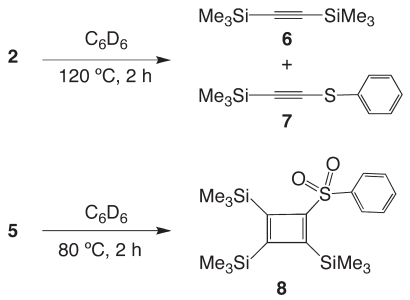
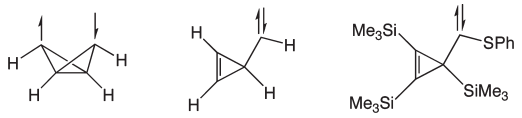


Chart 1. *exo,exo*-Bicyclo[1.1.0]butane-2,4-diyl 9, Cycloprop-3-enemethylene 10, and Sulfur-Substituted Cycloprop-3-enemethylene Derivative 11



of **2** and **5** calculated at the B3LYP/6-31G(d) level are shown in Figure 4. This also shows that **5** does not exhibit $\sigma-\pi$ conjugation, whereas **2** shows conjugation between the σ orbital of the tetrahedrane core and the lone-pair electrons on the sulfur atom in **2**. These results are in agreement with the UV−vis absorption spectra of **2** and **5**.

We also carried out thermal reactions of **2** and **5**. Tetrahedranyl sulfide **2** decomposed into two acetylene molecules, bis(trimethylsilyl)acetylene (**6**) and phenyl trimethylsilylethynyl sulfide (**7**), when a solution of **2** in benzene at 120 °C in a sealed tube was heated (Scheme 3).[15] In contrast, tetrahedranyl sulfone **5** isomerized to the corresponding cyclobutadiene **8** when a solution of **5** in benzene was heated at 80 °C (Scheme 3).[15] Schreiner and co-workers[16] performed theoretical calculations on the isomerization of the parent tetrahedrane (C_4H_4), and they showed that *exo,exo*-bicyclo[1.1.0]butane-2,4-diyl (**9**) is the intermediate for isomerization of tetrahedrane to give cyclobutadiene, whereas cycloprop-3-enemethylene (**10**) is the intermediate for breaking tetrahedrane to give two acetylene molecules (Chart 1). From consideration of this calculation, the thermal reaction of **2**, which undergoes fragmentation into two acetylene molecules, can probably be explained by the fact that lone pairs on the sulfur atom stabilize the carbene center[17] of cycloprop-3-enemethylene derivative **11** to afford two acetylene molecules. Thus, it is quite reasonable to assume that **5** isomerized to the corresponding cyclobutadiene **8** because **5** has no lone pairs on the sulfur atom, which means that the carbene intermediate cannot be stabilized.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and spectral data for **2**, **3**, **4**, and **5**; thermal reactions of **2** and **5**; computational results on **2** and **5**; ORTEP drawing of **4**; and crystallographic data including atomic positional and thermal parameters for **3**, **4**, and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) For reviews of tetrahedrane, see: (a) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309. (b) Maier, G. *Pure Appl. Chem.* **1991**, *63*, 275. (c) Lee, V. Ya.; Sekiguchi, A. In *Strained Hydrocarbons*; Dodziuk, H., Ed.; Wiley-VCH: Weinheim, Germany, 2009; Chapter 2.

(2) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157.

(3) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1973**, *95*, 2738.

(4) (a) Peterson, R. F., Jr.; Baker, R. T. K.; Wolfgang, R. L. *Tetrahedron Lett.* **1969**, *10*, 4749. (b) Shevlin, P. B.; Wolf, A. P. *J. Am. Chem. Soc.* **1970**, *92*, 406. (c) Rodewald, L. B.; Lee, H. *J. Am. Chem. Soc.* **1973**, *95*, 623. (d) Maier, G.; Hoppe, M.; Lanz, K.; Reisenauer, H. P. *Tetrahedron Lett.* **1984**, *25*, 5645.

(5) (a) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520. (b) Maier, G.; Pfriem, S.; Schäfer, U.; Malsch, K.-D.; Matusch, R. *Chem. Ber.* **1981**, *141*, 3965.

(6) Maier, G.; Neudert, J.; Wolf, O.; Pappusch, D.; Sekiguchi, A.; Tanaka, M.; Matsuo, T. *J. Am. Chem. Soc.* **2002**, *124*, 13819.

(7) (a) Maier, G.; Neudert, J.; Wolf, O. *Angew. Chem., Int. Ed.* **2001**, *40*, 1674. (b) Sekiguchi, A.; Tanaka, M.; Matsuo, T.; Watanabe, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 1675.

(8) For recent reviews of silyl-substituted cyclobutadienes, see: (a) Matsuo, T.; Sekiguchi, A. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 211. (b) Sekiguchi, A.; Matsuo, T. *Synlett* **2006**, 2683.

(9) (a) Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6814. (b) Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 4412. (c) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3811.

(10) (a) Sekiguchi, A.; Tanaka, M. *J. Am. Chem. Soc.* **2003**, *125*, 12684. (b) Tanaka, M.; Sekiguchi, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 5821.

(11) Nakamoto, M.; Inagaki, Y.; Nishina, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2009**, *131*, 3172.

(12) For experimental procedures, spectral data for **2**−**5**, computational results for **2** and **5**, and crystal data for **3**−**5**, see the Supporting Information.

(13) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(14) Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: Oxford, U.K., 1998.

(15) For the experimental procedures of the thermal reactions of **2** and **5**, see the Supporting Information.

(16) Nemirowski, A.; Reisenauer, H. P.; Schreiner, P. R. *Chem.—Eur. J.* **2006**, *12*, 7411.

(17) (a) Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *Liebigs Ann.* **1997**, 365. (b) Kassaee, M. Z.; Shakib, F. A.; Momeni, M. R.; Ghambarian, M.; Musavi, S. M. *Tetrahedron* **2009**, *65*, 10093. (c) Kassaee, M. Z.; Shakib, F. A.; Momeni, M. R.; Ghambarian, M.; Musavi, S. M. *J. Org. Chem.* **2010**, *75*, 2539.