Structural Influence of a Sulfonyl Group in Eight-Membered Rings of Diorganosilanes[1]

A. Chandrasekaran, Roberta O. Day, and Robert R. Holmes*

Department of Chemistry, Box 34510, University of Massachusetts, Amherst, Massachusetts 01003-4510

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The new monocyclic diorganosilanes $O_2S(Me_2C_6H_2O)_2SiMe_2$ (**1**) and $O_2S[(t\text{-Bu})MeC_6H_2O]_2$-$SiR_2$, where R = Me (**2**) and R = Ph (**3**), were prepared by a condensation reaction of the appropriate diorganodichlorosilane with either one of the new diols $O_2S(Me_2C_6H_2OH)_2$ (**5**) and $O_2S[(t\text{-Bu})MeC_6H_2OH]_2$ (**6**) in ether solution in the presence of Et_3N. X-ray crystallographic studies showed that silane **1** has the eight-membered ring in an *anti* chairlike conformation, whereas silanes **2** and **3** have the eight-membered rings in *syn* boatlike conformations. Oxygen donor coordination to silicon is evident for **2** and **3** from one of the ring sulfonyl oxygen atoms in each. As a result, **1** remains tetracoordinate while **2** and **3** are pentacoordinate with trigonal-bipyramidal geometry. Likewise, the cyclic disiloxane $\{O_2S[(t\text{-Bu})MeC_6H_2O]_2Si(OH)\}_2O$ (**4**), prepared as a hydrolysis product, possesses a similar pentacoordinate structure at each of the silicon centers. VT ^{1}H NMR spectra for **1** and **2** indicate the presence of fluxional molecules where ring pseudorotation takes place, similar to that for cyclohexane. Activation energies of 9.1 and 11.0 kcal/mol were obtained for **1** and **2**, respectively. ^{13}C and ^{29}Si NMR data also were recorded. The [29]Si chemical shifts are indicative of the types of ligands attached to silicon.

Introduction

In the preceding article,[2] we found that incorporation of a sulfinyl group as a bridging ligand between aryl groups that comprised an eight-membered ring when coordinated to diorganosilanes gave molecular structures with no evidence for increased coordination from donor action to silicon from either the sulfur atom or the oxygen atom. All of the structures had long Si−S and Si−O distances, in the ranges 3.615(1)−3.645(3) and 5.095(2)−5.121(6) Å, respectively. These results contrast with those for a series of cyclic diorganosilanes[3,4] that had a sulfur atom in place of the sulfinyl group in the eight-membered-ring system. Here, sulfur donor action to silicon led to increased coordination and provided a series of geometries along a coordinate from a tetrahedron (T_d) toward a trigonal bipyramid (TBP). The Si−S distances ranged from 2.978(4) to 3.292(1) Å for members exhibiting this coordination. Linear interpolation between the Si−S van der Waals sum of 3.90 Å[5] and the sum of covalent radii of 2.20 Å[6] gave a displacement T_d → TBP ranging from 36% to 54%.[1b] Representative examples of each of these classes of silanes are **A**[2] and **B**.[4]

We first studied the sulfur-containing eight-membered-ring system in pentaoxyphosphoranes, where P−S donor action produced hexacoordinated structures in a series

Si–S 3.615(1)Å
Si–O 5.102(2)Å

A[2]

Si–S 3.074(1)Å

B[4]
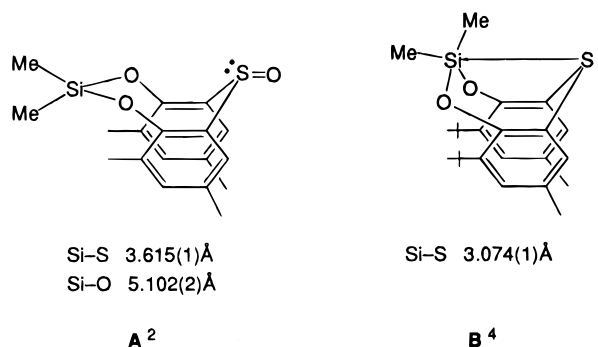
of geometries displaced along a coordinate from square pyramidal toward octahedral over a range of 44% to 70%.[7−11] A representative member is **C**.[8]

C[8]
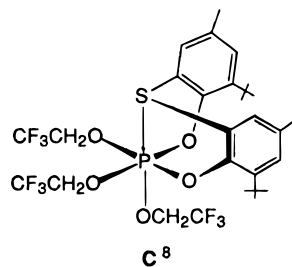
P–S = 2.362(2)Å

P–S $\begin{cases} \Sigma \text{ cov radii} = 2.14\text{Å}^6 \\ \Sigma \text{ van der Waals' radii} = 3.75\text{Å}^5 \end{cases}$

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(1) (a) Pentacoordinated Molecules. 107. (b) Part 106: Timosheva, N. V.; Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 3614.

(2) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1996**, *15*, 3182.

(3) Day, R. O.; Prakasha, T. K.; Holmes, R. R.; Eckert, H. *Organometallics* **1994**, *13*, 1285.

(4) Prakasha, T. K.; Srinivasan, S.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 10003.

(5) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(6) Sutton, L., Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions;* Special Publication Nos. 11 and 18; The Chemical Society: London, 1958 and 1965.

(7) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1913.

(8) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Inorg. Chem.* **1993**, *32*, 4360.

(9) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 2690.

(10) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 3391.

(11) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *75*, 249.

It was decided to introduce a sulfonyl group in place of the sulfinyl group and examine its influence in the attainment of pentacoordination for silanes through donor action at silicon. For this purpose, the new diols **5** and **6** were synthesized, which then allowed the

1 **2**

3 **4**

5 **6**
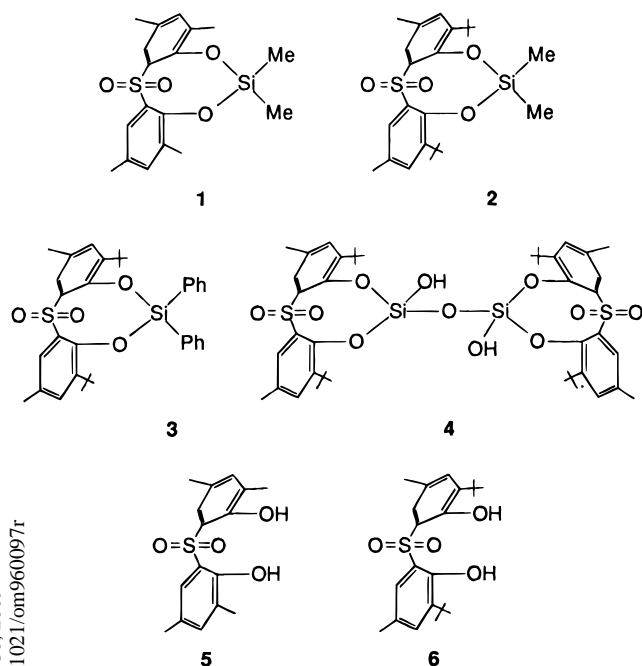
synthesis of the diorganosilanes **1**−**3**. Due to hydrolysis, **4** formed as a cyclic disiloxane containing the same ring system as is present in **1**−**3**. Structures of each of the new cyclic silicon compounds **1**−**4** were obtained by X-ray diffraction. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded as well to assess structural changes between the solid and solution states and to investigate the fluxional behavior of these molecules.

Experimental Section

2,4-Dimethylphenol (Fluka), dichlorodimethylsilane (Aldrich), and dichlorodiphenylsilane (Fluka) were used as supplied. 2,2′-Thiobis(4,6-dimethylphenol) (**7**) was synthesized according to a literature method.[12] Solvents were purified according to the standard procedures.[13] All the reactions involving silanes were carried out under a dry nitrogen atmosphere. Proton NMR spectra were recorded on a Bruker AC200 FT-NMR spectrometer. Solution ^{13}C and solution and solid-state ^{29}Si NMR spectra were recorded on Bruker MSL300 FT-NMR spectrometers. All the spectra were recorded in $CDCl_3$ except where noted. Solution chemical shifts are reported in ppm relative to tetramethylsilane. Solid-state chemical shifts are reported in ppm relative to $Me_3SiCH_2CH_2SO_3^-Na^+$. The latter is shifted upfield (−1.7 ppm) relative to TMS. Spectra were recorded at 23 °C, except in the VT ^{1}H NMR studies of **1** and **2**. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. Dioxythiobis(4,6-dimethylphenol), O_2S-$(Me_2C_6H_2OH)_2$ (5). To a solution of hydrogen peroxide (30%, 20.0 mL, 176 mmol) in glacial acetic acid (30 mL) was added 2,2′-thiobis(4,6-dimethylphenol) (**7**; 5.0 g, 18 mmol), and the suspension was heated for 2 h at about 100 °C. To the

(12) Pastor, S. D.; Denney, D. Z. *Phosphorus Sulfur Relat. Elem.* **1987**, *32*, 105.

(13) (a) Riddick, J. A., Bunger, W. B., Eds. Organic Solvents. In *Physical Methods in Organic Chemistry*; Wiley-Interscience: New York, 1970; Vol. II. (b) Vogel, A. I. *Textbook of Practical Organic Chemistry*; Longman: London, 1978.

resulting mixture was added 300 mL of water. The precipitate that formed was filtered, thoroughly washed with water, and dried: mp 220 °C (yield 5.2 g, 92%). ^{1}H NMR: 2.23 (s, 6 H, aryl−*Me*), 2.24 (s, 6 H, aryl−*Me*), 7.15 (s, 2 H, aryl), 7.22 (s, 2 H, aryl), 9.11 (s, 2 H, O*H*). ^{13}C NMR: 16.14, 20.56, 123.12, 125.35, 128.50, 129.88, 138.52, 151.59. Anal. Calcd for $C_{16}H_{18}O_4S$: C, 62.72; H, 5.92. Found: C, 62.30; H, 5.83.

Dioxythiobis(4-methyl-6-*tert*-butylphenol), $O_2S[(t\text{-Bu})$-$MeC_6H_2OH]_2$ (6). To a solution of 2-*tert*-butyl-4-methylphenol (84 g, 0.51 mol) in hexane (150 mL) was added 0.50 g of zinc chloride, and the mixture was cooled with ice. To this cold stirred solution was added a solution of sulfur dichloride (16 mL, 0.25 mol) in hexane (40 mL) over a period of 30 min. After the addition was complete, the solution was stirred at room temperature for 18 h. The yellow solution was filtered and the solvent removed from the filtrate to give a thick yellow oil. A solution of hydrogen peroxide (30%, 70 mL, 0.62 mol) in glacial acetic acid (70 mL) was added to the above oil, and the contents were heated at about 100 °C for 30 min. When the solution was cooled, some solid mass formed. The solution was decanted off and the solid extracted with hot acetone (500 mL). This solution on standing overnight with slow evaporation gave 33.5 g of crystalline solid. A further quantity of 25 g was obtained from the mother liquor as a second crop: mp 131−133 °C (yield 58.5 g, 60.0%). ^{1}H NMR: 1.40 (s, 18 H, *t*-Bu), 2.24 (s, 6 H, aryl−*Me*), 7.27 (s, 4 H, *aryl*), 9.52 (s, 2 H, O*H*). ^{13}C NMR: 20.93, 29.54, 35.55, 123.93, 125.51, 129.48, 134.84, 139.69, 152.53. Anal. Calcd for $C_{22}H_{30}O_4S$: C, 67.66; H, 7.74. Found: C, 67.61; H, 7.71.

{[Dioxythiobis(4,6-dimethyl-*o*-phenylene)]dioxy}-dimethylsilane, $O_2S[Me_2C_6H_2O]_2SiMe_2$ (1). A solution of **5** (2.6 g, 8.3 mmol) and dimethyldichlorosilane (1 mL) in ether (75 mL) was added together with a solution of triethylamine (2.4 mL, 17 mmol) in ether (50 mL) over a period of 50 min. This mixture was stirred for a further period of 48 h and the solution filtered. The filtrate was left under a nitrogen flow to get a crystalline product: mp 220−222 °C (yield 1.4 g, 46%). ^{1}H NMR ($CDCl_3$): 0.43 (s, 6 H, Si-*Me*), 2.19 (s, 6 H, aryl-*Me*), 2.29 (s, 6 H, aryl−*Me*), 7.18 (s, 2 H, aryl), 7.63 (s, 2 H, aryl). ^{1}H NMR (CD_2Cl_2, 260 K): 0.38, 2.18, 2.27, 7.21, 7.56. ^{1}H NMR (CD_2Cl_2, 185 K): 0.02, 0.58, 2.12, 2.22, 7.19, 7.52. ^{13}C NMR: −1.55, 16.57, 20.67, 127.79, 131.08, 131.74, 132.07, 137.33, 148.51. ^{29}Si NMR: −6.2. ^{29}Si NMR (solid): −16.51. Anal. Calcd for $C_{18}H_{22}O_4SSi$: C, 59.64; H, 6.12. Found: C, 59.78; H, 6.14.

{[Dioxythiobis(4-methyl-6-*tert*-butyl-*o*-phenylene)]-dioxy}dimethylsilane, $O_2S[(t\text{-Bu})MeC_6H_2O]_2SiMe_2$ (2). The procedure was similar to the synthesis of **1**. The quantities used were as follows: **6** (3.3 g, 8.3 mmol), Me_2SiCl_2 (1.0 mL, 8.2 mmol), and triethylamine (2.4 mL, 17 mmol). Mp: 202−206 °C (yield 1.9 g, 52%). ^{1}H NMR ($CDCl_3$): 0.55 (s, 6 H, Si−*Me*), 1.38 (s, 18 H, *t*-Bu), 2.32 (s, 6 H, aryl−*Me*), 7.33 (s, 2 H, aryl), 7.66 (s, 2 H, aryl). ^{1}H NMR (CD_2Cl_2, 295 K): 0.51, 1.38, 2.32, 7.39, 7.63. ^{1}H NMR (CD_2Cl_2, 200 K): 0.11, 0.65, 1.30, 2.27, 7.35, 7.58. ^{13}C NMR: 1.63, 20.97, 30.50, 35.36, 126.55, 128.2, 130.97, 134.18, 141.53, 150.03. ^{29}Si NMR: −8.43. ^{29}Si NMR (solid): −22.01. Anal. Calcd for $C_{24}H_{34}O_4SSi$: C, 64.53; H, 7.67. Found: C, 64.60; H, 7.56.

{[Dioxythiobis(4-methyl-6-*tert*-butyl-*o*-phenylene)]-dioxy}diphenylsilane, $O_2S[(t\text{-Bu})MeC_6H_2O]_2SiPh_2$ (3). The procedure was similar to the synthesis of **1**. The quantities used were as follows: **6** (0.94 g, 2.4 mmol), Ph_2SiCl_2 (0.50 mL, 2.4 mmol), and triethylamine (0.7 mL, 5.0 mmol). Mp: 238−240 °C (yield 0.50 g, 36%). ^{1}H NMR: 1.13 (s, 18 H, *t*-Bu), 2.34 (s, 6 H, aryl−*Me*), 7.30−7.71 (m, 14 H, aryl). ^{13}C NMR: 21.00, 30.95, 35.44, 127.88, 128.38, 130.81, 131.35, 134.52, 134.74, 135.20, 141.63, 149.67. ^{29}Si NMR: −42.81. Anal. Calcd for $C_{34}H_{38}O_4SSi$: C, 71.54; H, 6.71. Found: C, 71.55; H, 6.70.

Oxobis{[(dioxythiobis(4-methyl-6-*tert*-butyl-*o*-phenylene))dioxy]hydroxysilane}, $\{O_2S[(t\text{-Bu})MeC_6H_2O]_2Si$-$(OH)\}_2O$ (4). A solution of $SiCl_4$ (0.50 mL, 4.4 mmol) and **6** (3.4 g, 8.7 mmol) in toluene (100 mL) was added together with

Table 1. Crystallographic Data for Compounds 1−4

	1	2	3	4
formula	$C_{18}H_{22}O_4SSi$	$C_{24}H_{34}O_4SSi$	$C_{34}H_{38}O_4SSi$	$C_{44}H_{58}O_{11}S_2Si_2 \cdot C_4H_{10}O$
fw	362.51	446.66	570.79	957.32
cryst system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
cryst size (mm)	$0.30 \times 0.52 \times 0.80$	$0.45 \times 0.60 \times 0.65$	$0.22 \times 0.35 \times 0.62$	$0.45 \times 0.50 \times 0.60$
a (Å)	7.817(2)	9.580(1)	10.354(2)	9.9039(9)
b (Å)	9.221(1)	9.642(2)	10.388(2)	12.093(1)
c (Å)	12.943(2)	14.056(2)	14.820(4)	12.287(1)
α (deg)	89.96(1)	82.48(1)	91.89(2)	70.81(1)
β (deg)	98.65(2)	71.14(1)	90.64(2)	78.465(8)
γ (deg)	90.87(2)	84.71(1)	108.52(1)	70.307(9)
V (Å³)	922.2(3)	1216.4(3)	1510.2(6)	1301.9(2)
Z	2	2	2	1
D_{calc} (g/cm³)	1.305	1.220	1.255	1.221
$\mu_{\text{Mo K}\bar\alpha}$ (cm⁻¹)	2.59	2.09	1.84	2.05
total no. of rflns	2114	2777	3454	2983
no. of reflns with $I > 2\sigma_I$	1852	2460	2523	2472
R^a	0.0357	0.0355	0.0472	0.0440
$R_w{}^b$	0.0995	0.0924	0.1138	0.1267

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w(F_o{}^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^4]^{1/2}$.

a solution of triethylamine (0.70 mL, 5.0 mmol) in toluene (20 mL) at about 5 °C over a period of 20 min. The mixture was stirred at room temperature for 7 h and refluxed for 16 h. The solvent was removed under vacuum and the residue extracted with ether (125 mL). To the extract was added hexane (100 mL), and this mixture was kept for slow evaporation under a nitrogen flow to give crystals of **4**: mp >250 °C (yield 0.40 g, 11%). ^{1}H NMR: 1.29 (s, 36 H, *t*-Bu), 2.32 (s, 12 H, aryl−*Me*), 4.51 (s. br, O*H*), 7.33 (s, 4 H, aryl), 7.63 (s, 4 H, aryl). ^{29}Si NMR: −102.80. Anal. Calcd for $C_{44}H_{58}O_{11}S_2Si_2 \cdot C_4H_{10}O$: C, 60.22; H, 7.16. Found: C, 60.36; H, 7.14.

X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Details of the experimental procedures have been described previously.[14] The colorless crystals were mounted in thin-walled glass capillaries, which were sealed to protect the crystals from the atmosphere as a precaution. Data were collected using the θ−2θ scan mode with $3° \leq 2\theta_{\text{Mo K}\bar\alpha} \leq 43°$ at 23 ± 2 °C. No corrections were made for absorption. All of the data were included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least squares. Refinements were based on F^2, and computations were performed on a 486/66 computer using SHELXS-86 for solution[15] and SHELXL-93 for refinement.[16] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded carbon atoms. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$. Crystallographic data are summarized in Table 1.

Results and Discussion

The atom labeling schemes for **1**−**4** are given in the plots of Figures 1−4, respectively. Selected bond parameters are presented in Tables 2−5 for **1**−**4**, respectively. All figures are SNOOPI diagrams with thermal ellipsoids at the 50% probability level.

Syntheses. The new diols **5** and **6** were prepared by oxidation reactions with hydrogen peroxide in glacial acetic acid. For the synthesis of **5**, 2,2′-thiobis(4,6-
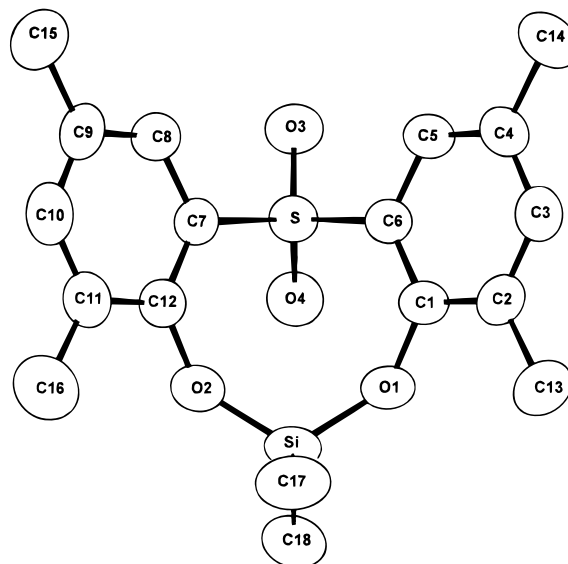
(14) Sau, A. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3076.

(15) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(16) Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany 1993.

Figure 1. Molecular geometry and atom-labeling scheme for $O_2S(Me_2C_6H_2O)_2SiMe_2$ (**1**) with hydrogen atoms omitted for clarity.
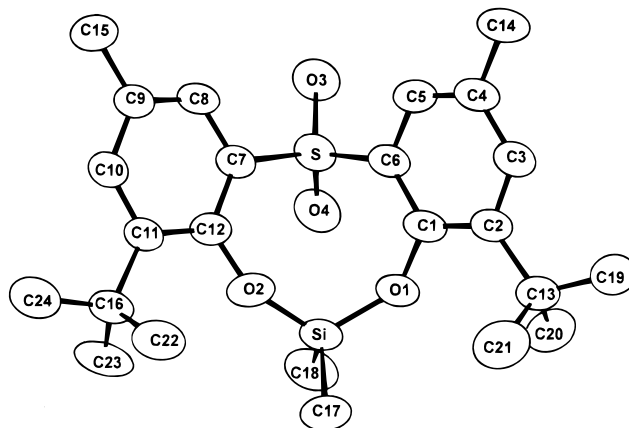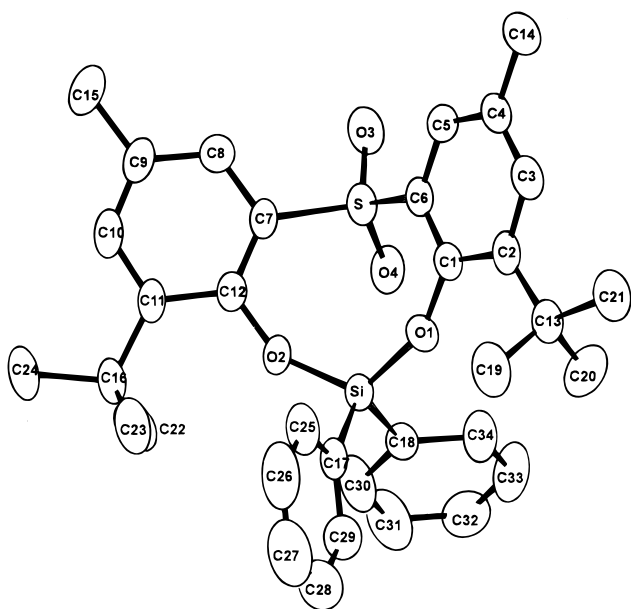

Figure 2. Molecular geometry and atom-labeling scheme for $O_2S[(t\text{-Bu})MeC_6H_2O]_2SiMe_2$ (**2**) with hydrogen atoms omitted for clarity.

dimethylphenol) (**7**) was oxidized. In the case of **6**, 2,2′-thiobis(4-methyl-6-*tert*-butylphenol) was prepared in hexane solution by a literature method.[9] After solvent

Figure 3. Molecular geometry and atom-labeling scheme for $O_2S[(t\text{-Bu})MeC_6H_2O]_2SiPh_2$ (**3**) with hydrogen atoms omitted for clarity.
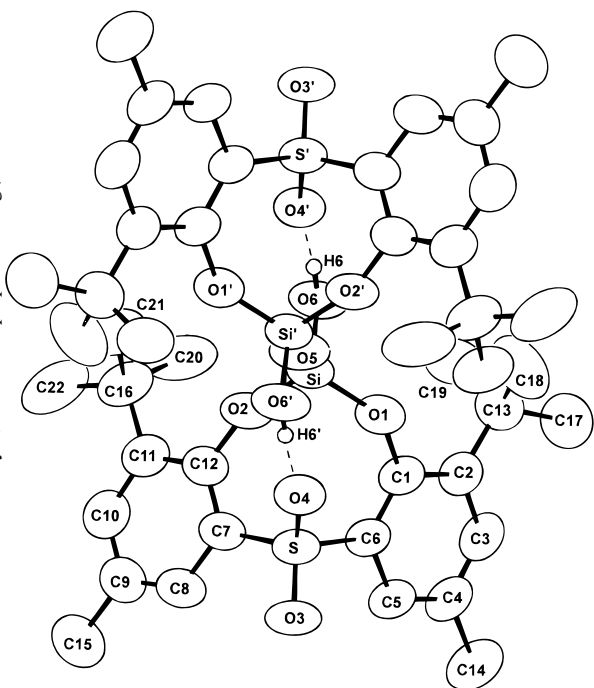
Figure 4. Molecular geometry and atom-labeling scheme for $\{O_2S[(t\text{-Bu})MeC_6H_2O]_2Si(OH)\}_2O$ (**4**) with hydrogen atoms omitted for clarity. Hydrogen bonds are shown as dashed lines. The primed atoms are generated by $-x$, $-y$, $-z$.

removal, the phenol was then oxidized with hydrogen peroxide in a manner similar to the procedure used for the synthesis of **6**.

The preparation of the monocyclic diorganosilanes **1**–**3** followed a condensation reaction of the appropriate diorganodichlorosilane with one of the diols, **5** or **6**, in ether solution in the presence of Et_3N. Yields ranged from 36 to 52%. Synthesis of the cyclic siloxane **4** proceeded by way of a similar condensation reaction of the diol **6** with $SiCl_4$ in toluene solution accompanied by hydrolysis to give a 11% yield. Equation 1 summarizes the reaction leading to **4**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $O_2S(Me_2C_6H_2O)_2SiMe_2$ (1)[a]

S–O(4)	1.430(2)	Si–C(17)	1.843(4)
S–O(3)	1.438(2)	Si–O(4)	3.237(2)
S–C(7)	1.766(3)	O(1)–C(1)	1.373(3)
S–C(6)	1.768(3)	O(2)–C(12)	1.372(3)
Si–O(1)	1.637(2)	C(1)–C(6)	1.388(4)
Si–O(2)	1.638(2)	C(7)–C(12)	1.390(4)
Si–C(18)	1.827(3)		
O(4)–S–O(3)	118.06(13)	O(1)–Si–O(4)	61.07(9)
O(4)–S–C(7)	110.85(13)	O(2)–Si–O(4)	61.98(9)
O(3)–S–C(7)	107.03(13)	C(18)–Si–O(4)	89.73(14)
O(4)–S–C(6)	110.02(13)	C(17)–Si–O(4)	155.08(13)
O(3)–S–C(6)	106.74(13)	C(1)–O(1)–Si	137.1(2)
C(7)–S–C(6)	103.00(13)	C(12)–O(2)–Si	136.7(2)
O(1)–Si–O(2)	113.43(11)	S–O(4)–Si	95.11(10)
O(1)–Si–C(18)	105.37(14)	O(1)–C(1)–C(6)	121.6(3)
O(2)–Si–C(18)	105.9(2)	C(1)–C(6)–S	122.8(2)
O(1)–Si–C(17)	108.3(2)	C(12)–C(7)–S	123.0(2)
O(2)–Si–C(17)	108.7(2)	O(2)–C(12)–C(7)	121.4(3)
C(18)–Si–C(17)	115.2(2)		

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 1.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $O_2S[(t\text{-Bu})MeC_6H_2O]_2SiMe_2$ (2)[a]

S–O(3)	1.431(2)	Si–C(17)	1.844(3)
S–O(4)	1.435(2)	Si–O(4)	2.841(2)
S–C(7)	1.759(2)	O(1)–C(1)	1.367(3)
S–C(6)	1.761(3)	O(2)–C(12)	1.360(3)
Si–O(2)	1.620(2)	C(1)–C(6)	1.397(3)
Si–O(1)	1.637(2)	C(7)–C(12)	1.397(3)
Si–C(18)	1.841(3)		
O(3)–S–O(4)	117.92(12)	O(2)–Si–O(4)	75.61(8)
O(3)–S–C(7)	107.05(11)	O(1)–Si–O(4)	71.64(8)
O(4)–S–C(7)	108.70(11)	C(18)–Si–O(4)	74.39(13)
O(3)–S–C(6)	106.92(11)	C(17)–Si–O(4)	177.23(13)
O(4)–S–C(6)	108.91(11)	C(1)–O(1)–Si	141.6(2)
C(7)–S–C(6)	106.82(11)	C(12)–O(2)–Si	154.2(2)
O(2)–Si–O(1)	113.44(10)	S–O(4)–Si	102.35(9)
O(2)–Si–C(18)	113.29(13)	O(1)–C(1)–C(6)	121.2(2)
O(1)–Si–C(18)	111.10(13)	C(1)–C(6)–S	123.8(2)
O(2)–Si–C(17)	103.97(13)	C(12)–C(7)–S	122.0(2)
O(1)–Si–C(17)	106.22(13)	O(2)–C(12)–C(7)	121.2(2)
C(18)–Si–C(17)	108.2(2)		

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 2.
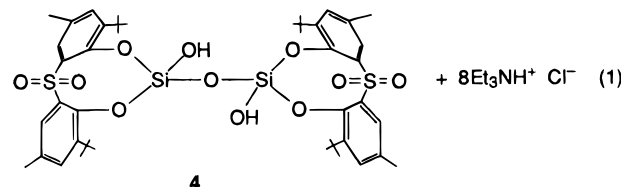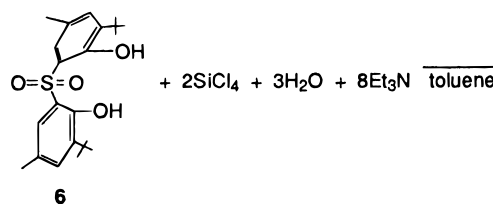
All of the compounds **1**–**4** are readily soluble in ether and can be crystallized from a mixture of ether and hexane by slow evaporation under a nitrogen flow.

Basic Structures. Three different structural types result from the X-ray analyses of **1**–**4**. The cyclic silane **1** is tetracoordinate (Figure 1) with the ring in an *anti* chairlike conformation where the silicon and sulfur atoms are on opposite sides of a plane formed by the remainder of the ring atoms (Figure 5). The Si–O(4) distance is 3.237(2) Å, which compares with 3.60 Å for

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for $O_2S[(t\text{-}Bu)MeC_6H_2O]_2SiPh_2$ (3)[a]**

S−O(3)	1.432(3)	Si−C(17)	1.860(4)
S−O(4)	1.432(3)	Si−O(4)	2.904(3)
S−C(7)	1.776(4)	O(1)−C(1)	1.360(4)
S−C(6)	1.776(4)	O(2)−C(12)	1.360(4)
Si−O(1)	1.630(3)	C(1)−C(6)	1.398(5)
Si−O(2)	1.632(3)	C(7)−C(12)	1.392(5)
Si−C(18)	1.854(4)		
O(3)−S−O(4)	117.8(2)	O(1)−Si−O(4)	72.07(11)
O(3)−S−C(7)	106.3(2)	O(2)−Si−O(4)	71.05(11)
O(4)−S−C(7)	108.5(2)	C(18)−Si−O(4)	75.58(13)
O(3)−S−C(6)	105.7(2)	C(17)−Si−O(4)	170.72(14)
O(4)−S−C(6)	108.1(2)	C(1)−O(1)−Si	152.1(2)
C(7)−S−C(6)	110.3(2)	C(12)−O(2)−Si	148.5(2)
O(1)−Si−O(2)	116.34(14)	S−O(4)−Si	100.82(13)
O(1)−Si−C(18)	109.9(2)	O(1)−C(1)−C(6)	121.2(3)
O(2)−Si−C(18)	108.6(2)	C(1)−C(6)−S	122.0(3)
O(1)−Si−C(17)	104.2(2)	C(12)−C(7)−S	122.6(3)
O(2)−Si−C(17)	104.1(2)	O(2)−C(12)−C(7)	121.2(3)
C(18)−Si−C(17)	113.7(2)		

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 3.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $\{O_2S[(t\text{-}Bu)MeC_6H_2O]_2Si(OH)\}_2O$ (4)[a]
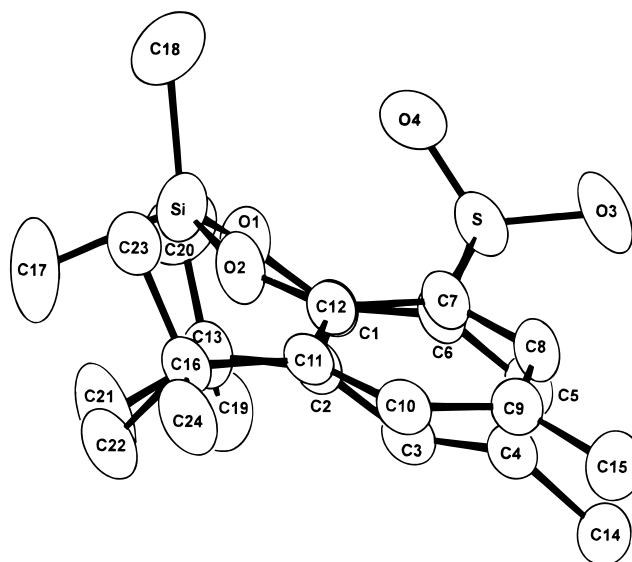
S−O(3)	1.434(2)	Si−O(1)	1.612(3)
S−O(4)	1.439(2)	Si−O(4)	2.898(3)
S−C(6)	1.768(4)	O(1)−C(1)	1.377(4)
S−C(7)	1.769(4)	O(2)−C(12)	1.359(4)
Si−O(5)	1.578(1)	C(1)−C(6)	1.394(5)
Si−O(2)	1.587(3)	C(7)−C(12)	1.383(5)
Si−O(6)	1.602(3)		
O(3)−S−O(4)	117.9(2)	O(5)−Si−O(4)	69.91(6)
O(3)−S−C(6)	107.5(2)	O(2)−Si−O(4)	76.44(11)
O(4)−S−C(6)	109.1(2)	O(6)−Si−O(4)	176.82(12)
O(3)−S−C(7)	107.3(2)	O(1)−Si−O(4)	71.46(10)
O(4)−S−C(7)	108.5(2)	C(1)−O(1)−Si	139.3(2)
C(6)−S−C(7)	105.9(2)	C(12)−O(2)−Si	155.7(3)
O(5)−Si−O(2)	113.78(13)	S−O(4)−Si	101.04(12)
O(5)−Si−O(6)	107.45(10)	Si−O(5)−Si′	180.0
O(2)−Si−O(6)	106.5(2)	O(1)−C(1)−C(6)	121.3(3)
O(5)−Si−O(1)	110.55(11)	C(1)−C(6)−S	124.6(3)
O(2)−Si−O(1)	110.0(2)	C(12)−C(7)−S	122.7(3)
O(6)−Si−O(1)	108.3(2)	O(2)−C(12)−C(7)	121.4(3)

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 4.
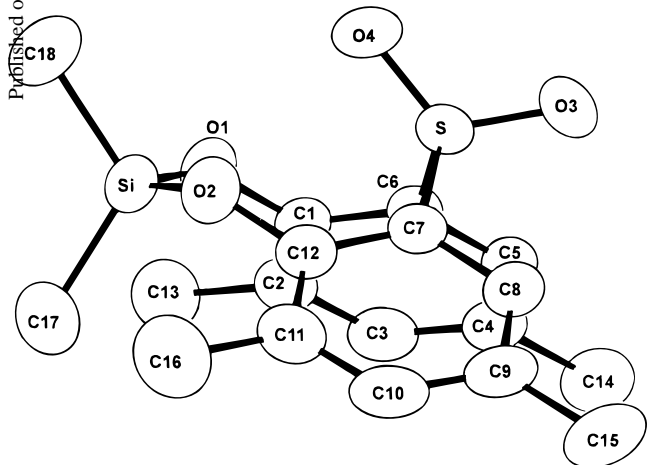
Figure 5. SNOOPI diagram showing an alternate view emphasizing the conformation of the eight-membered ring for $O_2S(Me_2C_6H_2O)_2SiMe_2$ (**1**).

Figure 6. SNOOPI diagram showing an alternate view emphasizing the conformation of the eight-membered ring for $O_2S[(t\text{-}Bu)MeC_6H_2O]_2SiMe_2$ (**2**).
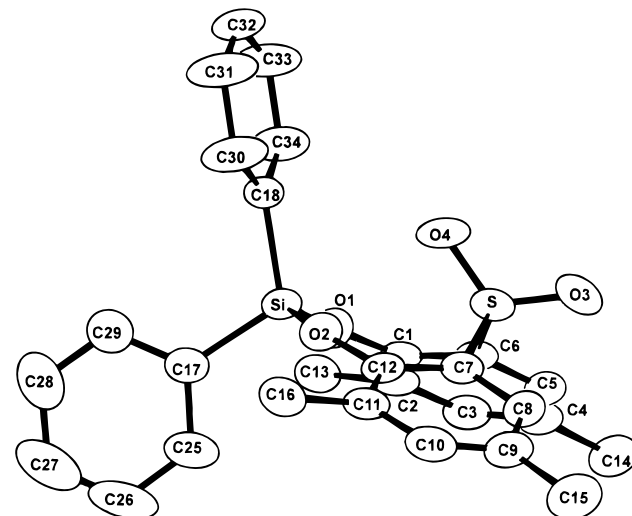
Figure 7. SNOOPI diagram showing an alternate view emphasizing the conformation of the eight-membered ring for $O_2S[(t\text{-}Bu)MeC_6H_2O]_2SiPh_2$ (**3**). Methyl carbons of the *tert*-butyl groups are omitted for clarity.

the sum of the van der Waals radii.[5] The Si−S distance is 3.653(1) Å.

Silanes **2** and **3**, which differ only in the acyclic substituents, have very closely related geometries with the rings in *syn* boatlike conformations. Both show an appreciable degree of donor action provided by one of the sulfonyl oxygen atoms, O(4) (Figures 2 and 3). These Si−O(4) distances are 2.841(2) Å for **2** and 2.904-(3) Å for **3**. The structures are displaced along a coordinate from a tetrahedron toward a trigonal bipyramid, $T_d \rightarrow$ TBP. This displacement amounts to 45% for **2** and 41% for **3** obtained by noting how far the Si−O(4) distances are displaced from the sum of the van der Waals radii toward the sum of the Si−O covalent radii of 1.91 Å.[6] Accordingly, the rings for **2** and **3** are in boatlike conformations (Figures 6 and 7), respectively). The Si−S distances are 3.445(1) Å for **2** and 3.470(2) Å for **3**. The partially formed trigonal bipyramid in each case has the ring oxygen atoms located in diequatorial positions along with one of the acyclic ligands. This leaves the other acyclic ligand and the donor oxygen atom situated at axial sites. This geometrical arrangement of ligands is the same as that found for cyclic silanes[1b,3,4] with a similar eight-

Table 6. Comparison of Si−O and Si−S Bond Parameters, Ring Conformations, and ^{29}Si Chemical Shifts for Cyclic Silanes

compd[a]	Si−O(4), Å	% TBP[b]	O(4)−Si−C$_{ax}$, deg[c]	Σ_{eq}, deg[c]	eight-membered ring conform.	$\delta(^{29}Si)$, ppm soln[d]	$\delta(^{29}Si)$, ppm solid
1	3.237(2)				*anti* (chair)	−6.2	−16.51[e]
3	2.904(3)	41.2	170.7(1)	334.8	twist *syn* (boat)	−42.81	
4	2.898(3)	41.5	176.8(1)	334.3	twist *syn* (boat)	−102.80	
2	2.841(2)	44.9	155.1(1)	337.8	twist *syn* (boat)	−8.43	−22.01[e]

compd[a]	Si−S, Å	% TBP[b]	S−Si−C$_{ax}$, deg[c]	Σ_{eq}, deg[c]	eight-membered ring conform.	$\delta(^{29}Si)$, ppm soln[d]	$\delta(^{29}Si)$, ppm solid
D	3.292(1)	35.8	164.1(1)	334.4(5)	twist *syn* (boat)	−13.22	
D	3.280(1)	36.5	166.8(1)	334.1(5)	twist *syn* (boat)		
B	3.074(1)	48.6	169.5(2)	341.4(3)	symmetrical *syn* (boat)	−13.51	
E (Si(1))	3.04(1)	50.6		345(1)	symmetrical *syn* (boat)		−107.84[f]
E (Si(2))	3.11(1)	46.5		339(1)	twist *syn* (boat)		−99.35[f]

[a] Data for **1**−**4** are taken from this work. The X-ray parameters and ^{29}Si NMR data for **E** are taken from ref 3. All the data for **B** and **D** are from ref 4. [b] Percent geometrical displacement from a tetrahedron to a trigonal bipyramid. [c] With reference to a TBP with O(4) or sulfur in an axial position and both ring oxygen atoms in equatorial positions. [d] All in CDCl$_3$ solution. [e] Relative to Me$_3$SiCH$_2$CH$_2$SO$_3^-$Na$^+$. [f] Relative to Me$_4$Si.
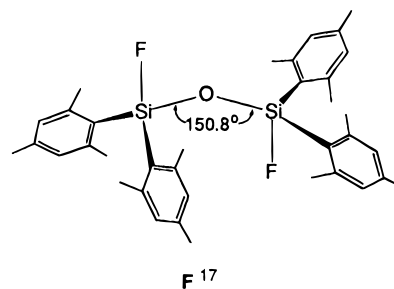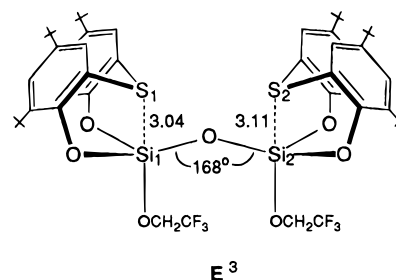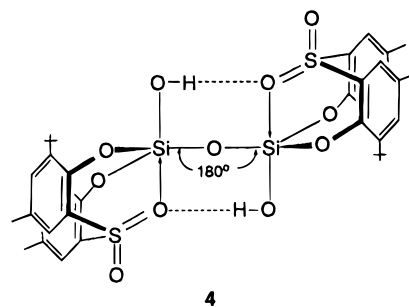
membered ring that has a sulfur atom in place of the sulfonyl group, for example, **D**.[4] Here the Si−S distance is 3.286(1) Å (average) and is calculated to be 36.2% displaced, $T_d \rightarrow$ TBP.

D [4]
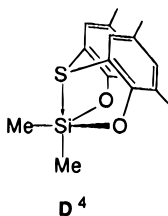
Although the cyclic disiloxane **4** represents a hydrolysis product (eq 1), the local structure around the silicon atoms is similar to that found for the cyclic silanes **2** and **3**. An inversion center which is located at O(5) (Figure 4) equates the geometrical arrangement about each silicon center. The ring conformation, which is in a boat-like form, allows oxygen donor action to silicon from the sulfonyl group. As a consequence, the geometry is approaching a trigonal bipyramid. From the Si−O(4) distance of 2.898(3) Å, a displacement $T_d \rightarrow$ TBP of 41.5% is calculated. The Si−S distance is 3.474(1) Å. Pertinent bond parameters summarizing these displacements, ring conformations, and ^{29}Si chemical shifts are compared in Table 6 for **1**−**4** along with comparable data for the related sulfur-containing cyclic silanes **B**[4] and **D**[4] and the cyclic disiloxane **E**.[3]

A further feature of interest for **4** is the presence of a hydrogen bond in the solid-state structure. The two hydrogen bonds are symmetrically related. They are located between the hydrogen atom on a hydroxy group attached to one of the silicon atoms and the oxygen atom of the sulfonyl group attached to the other silicon atom. This is the oxygen atom involved in Si−O donor action, *i.e.*, O(6)−H---O(4) in Figure 4. The O(6)−O(4) distance is 2.899(3) Å. The disiloxane angle associated with the Si−O(5)−Si′ atoms is required by symmetry to be 180°. The linearity followed here may be a result of the presence of the symmetrically placed hydrogen bond-interactions that couple the two silicon centers together. In the related disiloxane **E**,[3] containing the same type of eight-membered ring as present in **4** but lacking hydrogen bonding, the Si−O−Si angle is 168(2)°. Sulfur

coordination to silicon is present in **E**, giving $T_d \rightarrow$ TBP displacements of 46.5% and 50.6% for the two symmetrically different silicon atoms. In the acyclic disiloxane **F**,[17] lacking either hydrogen bonding or donor action promoting pentacoordination, the Si−O−Si angle is 150.8(2)°.

4

E [3]

F [17]

Structural Comparisons. We see that the use of a sulfonyl group in the cyclic components of **2**−**4** results in an increase in coordination geometry due to oxygen−

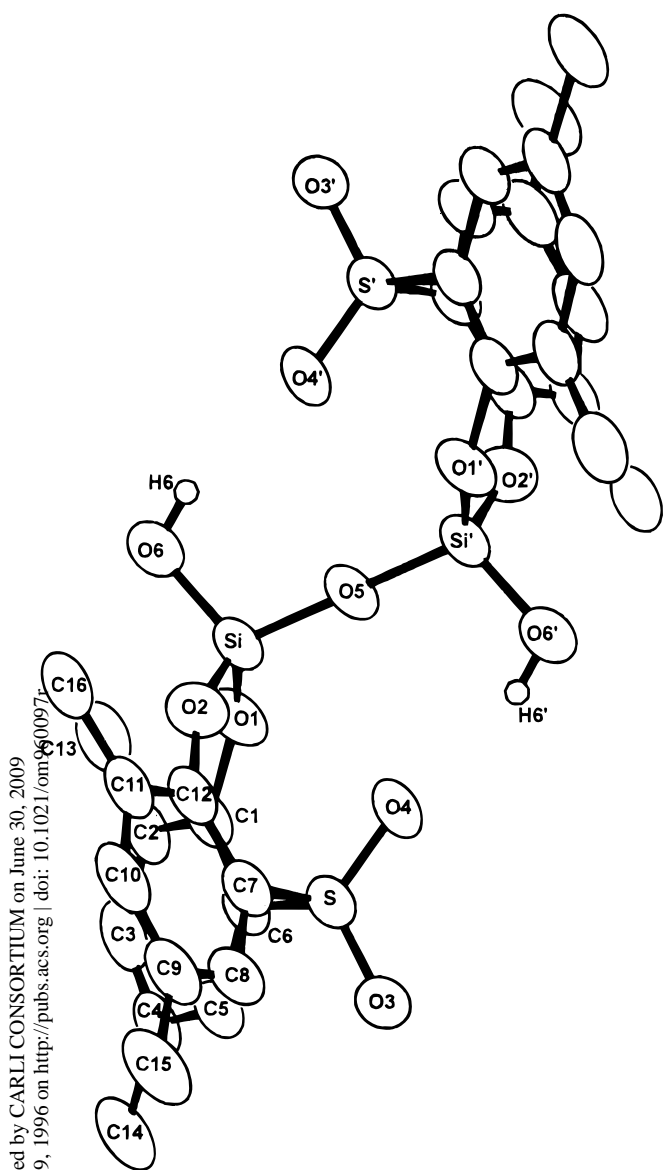(17) Johnson, S. E.; Deiters, J. A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 3250.
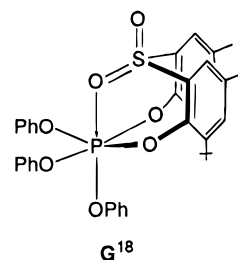
G[18]

P–O = 2.49Å

$$P-O \begin{cases} \Sigma cov\ radii = 1.83Å^{[6]} \\ \Sigma\ vdW\ radii = 3.35Å^{[5]} \end{cases}$$

ing to pentacoordination is present in **2**–**4**, no apparent reactivity difference is reflected relative to **1**, which remains tetracoordinated. Neither **1** nor **2** hydrolyzed in aqueous solution over a 1 week period at 25 °C. Also, in a boiling CDCl$_3$ solution, **2** did not show any evidence of reaction with catechol over a period of 2 h. It may be that the coordination is not strong enough to cause increased reactivity. Previous work leading to enhanced reactivity of pentacoordinated silicon relative to tetra-coordinated precursors has centered primarily on an-ionic five-coordinate silicon compounds,[19–21] where the coordinate bonds are presumed to be much stronger, as implied by their shorter bond distances.

VT ^{1}H NMR Spectroscopy. Figures 9 and 10 display variable-temperature ^{1}H NMR spectra for **1** and **2**, respectively. Unlike silane **A**,[2] which contains a ring sulfoxide group and possesses a temperature-invariant proton spectrum, both **1** and **2** show that the two methyl signals which are present at low temperatures coalesce to one signal at higher temperatures. In the case of **A**, the two methyl signals remained unchanged over the temperature range from 23 to 95 °C. This suggested the presence of a static structure for **A**. By way of contrast, the fluxional nature of **1** and **2** is consistent with ring pseudorotational behavior as illustrated in Scheme 1 for silane **1**. Here an *anti*–*anti* ring flipping is postulated for **1**. For **2**, a similar process of ring pseudorotation would involve *syn*–*syn* ring reorienta-tion. This is related to the chair–chair ring conforma-tional change in cyclohexane and related systems.[22] The lack of this type of process for **A** indicates an appreciable energy difference in the two ring conformations depicted in Scheme 1. For **A**, the sulfur atom has two different groups attached to it, the lone pair and an oxygen atom, which may provide for the more rigid behavior.

The activation energies obtained for **1** and **2** are 9.1 and 11.0 kcal/mol, respectively. The higher value for **2** may be due to the presence of Si–O coordination, which must be cleaved during the fluxional process; this would require additional energy compared to the process for **1**, where no such interaction is present.

^{29}Si NMR Chemical Shifts. Table 6 lists ^{29}Si chemical shifts for **1**–**4** for comparison with those for

Figure 8. SNOOPI diagram showing an alternate view emphasizing the conformation of the eight-membered ring for {O$_2$S[(*t*-Bu)MeC$_6$H$_2$O]$_2$Si(OH)}$_2$O (**4**). Methyl carbons of the *tert*-butyl groups are omitted for clarity. The primed atoms are generated by −*x*, −*y*, −*z*.

silicon donor action. This observation is in contrast to the lack of any such interaction for **1** or where the sulfoxide group was incorporated into the cyclic com-ponent of a series of silanes.[2] **A**[2] is shown in the Introduction as a representative member of this series. Although it is possible that silanes such as **A** could exhibit sulfur donor action, the basicity of the sulfur atom is no doubt sufficiently reduced so as to render such coordination unlikely, at least compared to silanes such as **B, D,** and **E** which have ring sulfur atoms acting as Lewis base donors to silicon atoms. As has been already noted, ring sulfur atoms also lead to an increase in coordination geometry in cyclic penta-oxyphosphoranes.[7–11] In this series, the structures are hexacoordinated as a result of phosphorus–silicon interactions.

Recently, we employed the sulfonyl group in eight-membered rings of pentaoxyphosphoranes. Similar to that found for **2**–**4**, oxygen coordination was apparent in **G**.[18] Even though oxygen–silicon donor action lead-

(18) Presented in part at the 211th National Meeting of the American Chemical Society, New Orleans, LA, March 24–28, 1996; INOR 189.

(19) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927 and references cited therein.

(20) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17 and references cited therein.

(21) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371 and references cited therein.

(22) Anet, F. A. L. Medium-sized Oxygen Heterocycles. In *Confor-mational Analysis of Medium-Sized Heterocycles*; Glass, R. S., Ed.; VCH: New York, 1988; Chapter 2.
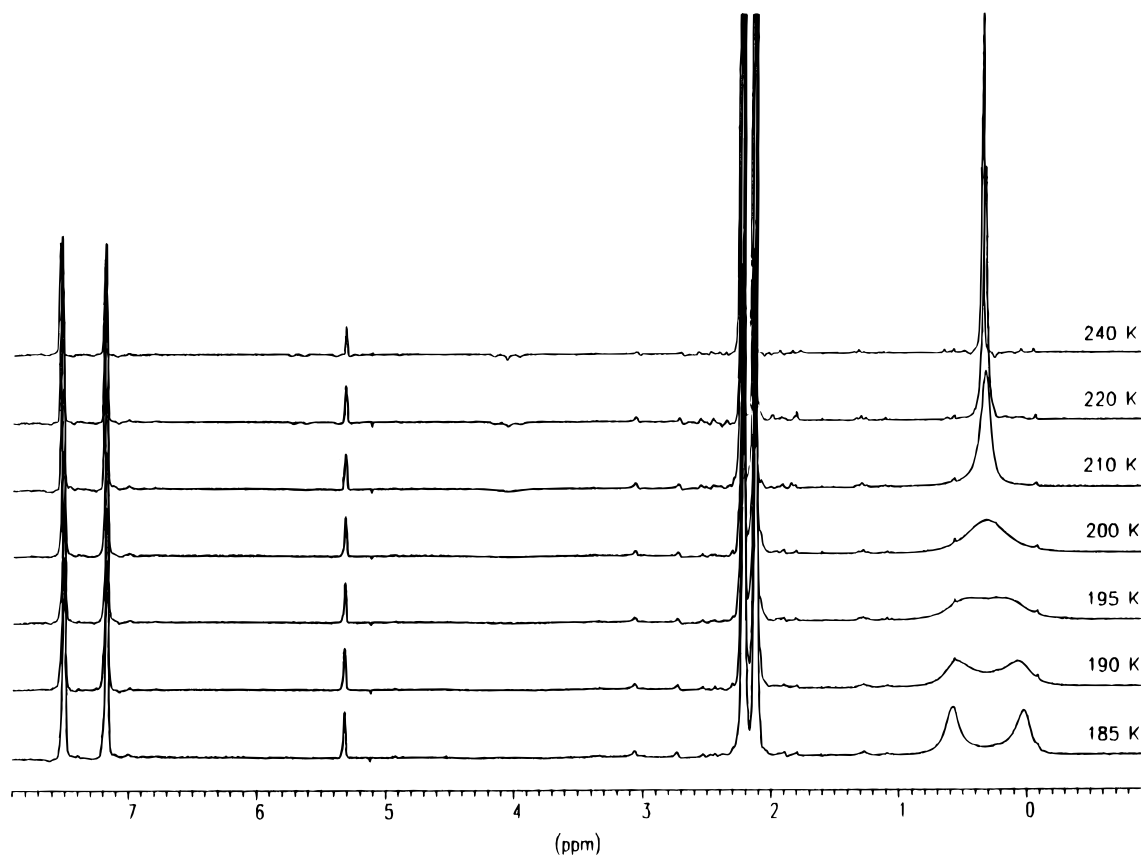
Figure 9. Variable-temperature ^1H NMR spectra for $O_2S(Me_2C_6H_2O)_2SiMe_2$ (**1**) showing the coalescence of the Si$-$Me$_2$ protons.
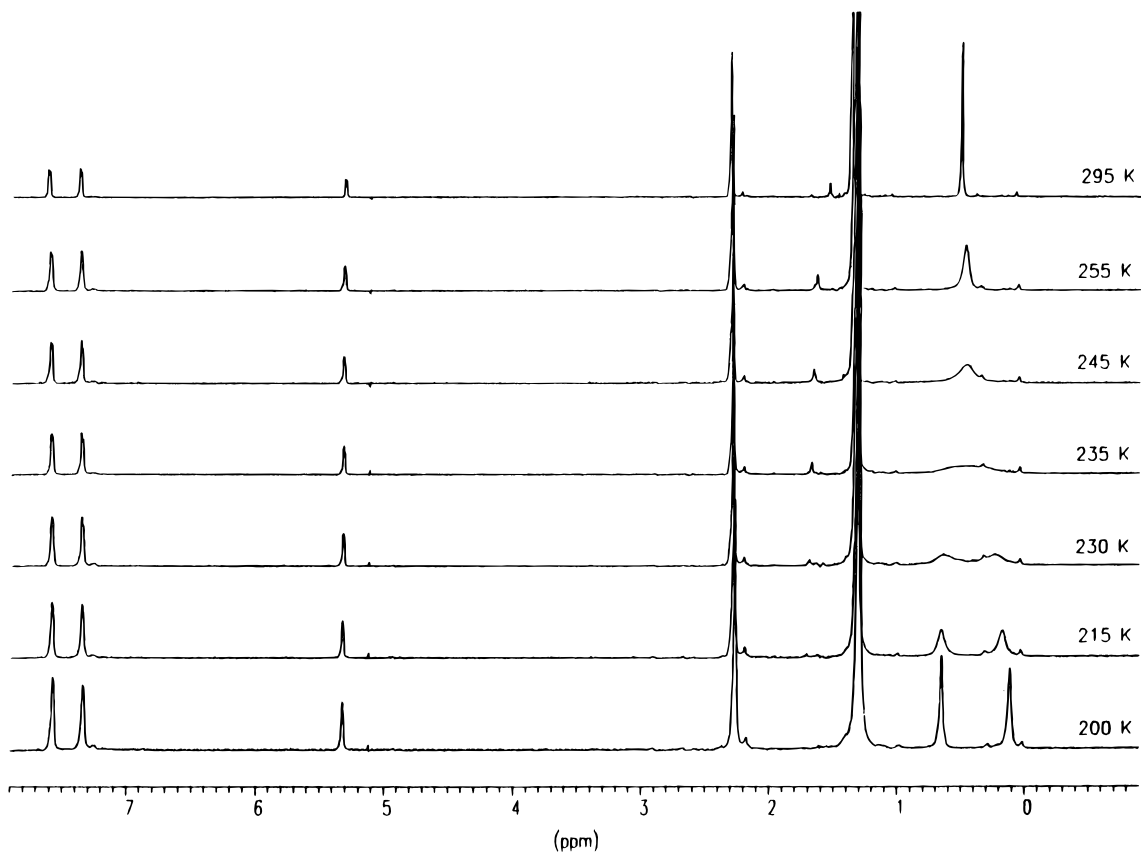
Figure 10. Variable-temperature ^1H NMR spectra for $O_2S[(t\text{-Bu})MeC_6H_2O]_2SiMe_2$ (**2**) showing the coalescence of the Si$-$Me$_2$ protons.

related cyclic silanes[3,4] that have ring sulfur atoms in place of the sulfonyl groups. There is no dependence of the ^{29}Si shifts with the degree of donor atom coordination apparent from these silanes. Silane **1**, which lacks

Scheme 1
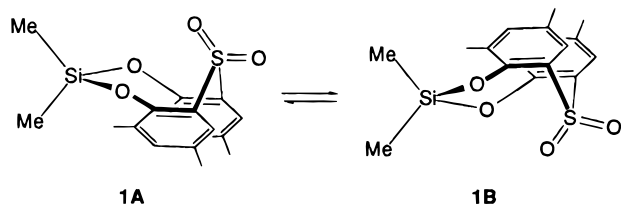
Si—O coordination with the ring in an *anti* chair formation, has a ^{29}Si shift of −6.2 ppm. This value is very close to that for **2** (−8.43 ppm), which exhibits a pentacoordinate geometry, 45% toward a TBP. The compositions of these two silanes differ only in the presence of *tert*-butyl groups *ortho* to the ring oxygen atoms in **2** in place of methyl groups similarly placed in **1**. This may be compared with the sulfur-containing rings for the silanes **D** and **B**, which have the same ring substituents as **1** and **2**. Here the ^{29}Si shifts, −13.51 and −13.22 ppm, respectively, are nearly identical. The solid-state ^{29}Si signals shift slightly upfield in comparison to the solution values for **1** and **2** (Table 6), with the pentacoordinated derivative **2** maintaining the higher upfield shift relative to the tetracoordinated silane **1**. These upfield shifts may be attributable to lattice effects, although no definitive information is provided on this point.

The increase in chemical shift for **3** to −42.81 ppm is attributable to the presence of electron-withdrawing phenyl groups attached to silicon in place of methyl groups found in **1, 2, D**, and **B**. Similarly, the solid-

state ^{29}Si shifts for the silicon atoms in the cyclic disiloxane **E**, −107.84 and −99.35 ppm, bracket those for the solution-state ^{29}Si shift of the related cyclic disiloxane **4**, −102.80 ppm. The larger shielding present in **E** and **4** compared to the other silanes in Table 6 is attributable to the presence of the larger number of electronegative oxygen atoms in these disiloxanes. Both **E** and **4** show pentacoordinate structures about halfway toward the TBP.

Conclusion. In contrast to silanes containing eight-membered rings with bridging sulfoxide groups that show no donor atom coordination at silicon, analogous cyclic silanes with ring sulfonyl groups in place of sulfoxide groups show oxygen—silicon coordination giving geometries that lie along a coordinate from tetrahedral to trigonal bipyramidal. These pentacoordinate structures compare with related cyclic silanes we studied earlier, where sulfur—silicon coordination was found that led to similar trigonal-bipyramidal formulations.

Supporting Information Available: Atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for **1** (Tables S1−S4), **2** (Tables S5−S8), **3** (Tables S9−S12), and **4** (Tables S13−S16) (17 pages). Ordering information is given on any current masthead page.