3182 *Organometallics* **1996,** *15,* 3182−3188

Structural Influence of a Sulfinyl Group in Eight-Membered Rings of Diorganosilanes

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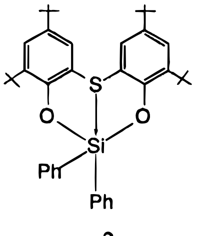
The new monocyclic diorganosilanes $OS(Me_2C_6H_2O)_2SiR_1R_2$, where $R_1 = R_2 =$ Me (**1**), $R_1 =$ Me, $R_2 =$ Ph (**2**), and $R_1 = R_2 =$ Ph (**3**), were prepared by a condensation reaction of oxythiobis(4,6-dimethylphenol), $OS(Me_2C_6H_2OH)_2$ (**4**), with the appropriate diorganodichlorosilane in CH_2Cl_2 solution in the presence of Et_3N. X-ray crystallographic studies showed that the silanes had the eight-membered rings positioned in *anti* chairlike conformations. This precluded any additional coordination at silicon with the sulfinyl group that was present as part of the ring system in each case. For silane **2** with two types of acyclic organo substituents attached to silicon, two isomers formed which differed in the position of these groups, *cis* or *trans*, relative to the ring sulfinyl group. ^{1}H, ^{13}C, and ^{29}Si solution state NMR spectral data were recorded. Temperature-dependent ^{1}H NMR data suggest a rigid ring conformation for **1**.

Introduction

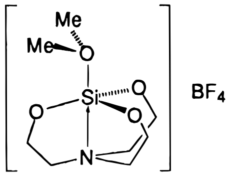
Previous work[1−3] on cyclic silanes having a sulfur atom as part of an eight-membered ring revealed the presence of sulfur−silicon coordination in a series of geometries that traversed a coordinate from tetrahedral toward trigonal bipyramidal, $T_d \rightarrow$ TBP. A representative member is the diphenyl silane **A**,[2] which has the ring in a *syn* boat conformation, *i.e.*, with the sulfur and silicon atom on the same side of the average plane of the remaining ring atoms. Two Si−S distances are observed due to the presence of two independent molecules per unit cell. Their values are 2.996(2) and 3.063(2) Å, which compares with the sum of covalent radii of 2.20 Å[4] and the sum of the van der Waals radii of 3.90 Å.[5] Simple interpolation gives the geometry of **A** as 51.1% $T_d \rightarrow$ TBP.[2]



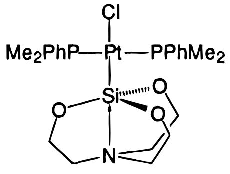
A 2

In accounting for the enhanced reactivity[6−8] of pentacoordinate silicon relative to related tetracoordinate members, it is important to understand the structural and theoretical basis[9,10] regarding their formation. The use of donor ligands of various kinds that promote increased coordination of silanes provides useful models for this purpose.[6−8] A survey of the literature[6] reveals quite a variety of organosilanes that undergo donor action with oxygen- and nitrogen-containing ligands leading to TBP geometries. In most cases, the incoming donor atom occupies an axial position of the trigonal bipyramid. Further, these compounds are monocyclic as a consequence of donor action. In the absence of donor action, the organosilanes would have only acyclic ligands.

Silatranes form an extensive class of substances, indicating varying degrees of nitrogen coordination[11−15] extending from 1.965(5) Å for **B**[16] to 2.89(1) Å for **C**.[17]



B 16



C 17

In these, a polycyclic ring is formed, similar to what we find in **A**, where the donor atom stems from part of a cyclic system.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

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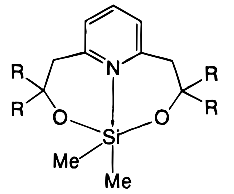
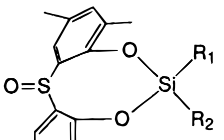
Unique are the pseudo-atranes **D**[18] and **E**,[19] which exhibit Si−N coordination in TBP geometries and have Si−N distances of 2.727(2) and 2.703(2) Å, respectively.



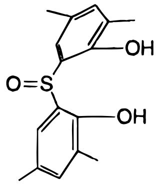
D [18] R, R = adamantyl
E [19] R = R = Ph

To extend the range of potential donor groups that might cause the formation of higher coordinate geometries for organosilanes, we decided to incorporate the sulfinyl group into the same type of eight-membered ring system as displayed for **A**.

For this purpose, it was necessary to synthesize the new diol **4**, which was used in the preparation of the diorganosilanes **1**−**3**. Two isomers were obtained for **2**. These isomers, **2A** and **2B**, along with **1** and **3** were subjected to X-ray analysis. An X-ray study of the diol **4** also was carried out for comparison. ^{1}H, ^{13}C, and ^{29}Si solution-state NMR data were recorded to assess possible changes relative to the solid-state structures.



	R_1	R_2
1	Me	Me
2A	Ph	Me
2B	Me	Ph
3	Ph	Ph



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Experimental Section

2,4-Dimethylphenol (Fluka) dichlorodimethylsilane (Aldrich), dichlorodiphenylsilane (Fluka), and dichloromethylphenylsilane (Fluka) were used as supplied. 2,2′-Thiobis(4,6-dimethylphenol) (**5**) was synthesized according to a literature method.[20] Solvents were purified according to standard procedures.[21] 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. Carbon-13 and silicon-29 NMR spectra were recorded on a Bruker MSL300 FT-NMR spectrometer. All the spectra were recorded in $CDCl_3$. Chemical shifts are reported in ppm, downfield positive, relative to tetramethylsilane. All were recorded at 23 °C unless otherwise mentioned. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory.

Syntheses. Oxythiobis(4,6-dimethylphenyl), $OS(Me_2C_6H_2OH)_2$ (4). A solution of hydrogen peroxide (30%, 20.0 mL, 176 mmol) in glacial acetic acid (10 mL) was added to a solution of 2,2′-thiobis(4,6-dimethylphenol) (**5**; 10 g, 36 mmol) in acetone (100 mL). This solution was heated for 2 h at about 50 °C. To the resulting mixture was added 300 mL of water. The powdery precipitate was filtered, thoroughly washed with water, and air-dried. This powder was washed with ether (200 mL) and dried under vacuum; mp 196 °C dec (yield 9.0 g, 85%). ^{1}H NMR: 2.20 (s, 6 H, aryl−*Me*), 2.22 (s, 6 H, aryl−*Me*), 6.78 (s, 2 H, aryl), 7.05 (s, 2 H, aryl), 8.95 (s, 2 H, O*H*). ^{13}C NMR: 15.43, 20.47, 123.79, 135.46, 122.14, 128.08, 129.23, 153.67. Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 66.12; H, 6.33.

{[Oxythiobis(4,6-dimethyl-*o*-phenylene)]dioxy}dimethylsilane, $OS(Me_2C_6H_2O)_2SiMe_2$ (1). To a solution of **4** (2.4 g, 8.3 mmol) and triethylamine (2.4 mL, 17 mmol) in dichloromethane (100 mL) was added a solution of Me_2SiCl_2 (1.0 mL, 8.2 mmol) in dichloromethane (10 mL). This mixture was stirred for a period of 24 h, and the solvent was removed under vacuum. The residue was extracted with ether (300 mL) and filtered. Solvent was removed from the filtrate, and the solid was recrystallized from a 1:1 hexane−dichloromethane mixture by slow evaporation under a nitrogen flow: mp 202−204 °C dec (yield 2.2 g, 77%). ^{1}H NMR: 0.02 (s, 3 H, Si−*Me*), 0.60 (s, 3H, Si−*Me*), 2.15 (s, 6 H, aryl−*Me*), 2.30 (s, 6 H, aryl−*Me*), 6.98 (s, 2 H, aryl), 7.50 (s, 2 H, aryl). ^{1}H NMR ($C_6D_5CD_3$ at 23 °C): −0.21 (s, 3 H, Si−*Me*), 0.37 (s, 3 H, Si−*Me*), 1.93 (s, 6 H, aryl−*Me*), 1.98 (s, 6 H, aryl−*Me*), 6.62 (s, 2 H, aryl), 7.87 (s, 2 H, aryl). ^{1}H NMR ($C_6D_5CD_3$ at 95 °C): −0.10 (s, 3 H, Si−*Me*), 0.41 (s, 3H, Si−*Me*), 1.98 (s, 6 H, aryl−*Me*), 2.04 (s, 6 H, aryl−*Me*), 6.70 (s, 2 H, aryl), 7.79 (s, 2 H, aryl). ^{13}C NMR: −3.61, −2.70, 15.84, 20.79, 121.08, 133.94, 128.98, 133.36, 137.08, 145.38. ^{29}Si NMR: −4.5. Anal. Calcd for $C_{18}H_{22}O_3SSi$: C, 62.39; H, 6.40. Found: C, 61.58; H, 6.54.

{[Oxythiobis(4,6-dimethyl-*o*-phenylene)]dioxy}phenylmethylsilane, $OS(Me_2C_6H_2O)_2Si(Me)Ph$ (2). The procedure was similar to the synthesis of **1**. The quantities used were as follows: **4** (1.8 g, 6.2 mmol), triethylamine (1.8 mL, 13 mmol), and $Me(Ph)SiCl_2$ (1.0 mL, 6.2 mmol) (yield 1.5 g, 70%). Anal. Calcd for $C_{23}H_{24}O_3SSi$: C, 67.61; H, 5.92. Found: C, 67.22; H, 6.05. The recrystallized product was extracted with ether (100 mL) to give a solution with an isomer ratio **2A**:**2B** of 2:1. Slow evaporation of this solution under a nitrogen flow gave only a small quantity of crystalline **2A**, which was separated by hand-picking: mp >180 °C dec. The residue left after the ether extract had some globular polycrystalline solid, which was hand-picked and found to be isomer **2B** (about 50 mg). This was crystallized from ether: mp 204−206 °C. Isomer **2A**: ^{1}H NMR 0.24 (s, 3 H, Si−*Me*), 2.25 (s, 6 H, aryl−*Me*), 2.33 (s, 6 H, aryl−*Me*), 7.04 (s, 2 H, aryl of diphenol), 7.95 (s, 2 H, aryl of diphenol), 7.45−7.55 (m, 5 H, phenyl); ^{13}C NMR −5.2, 15.7, 20.9, 120.8−145.7; ^{29}Si NMR −20.9. Isomer **2B**: ^{1}H NMR 0.90 (s, 3 H, Si−*Me*), 1.64 (s, 6 H, aryl−*Me*), 2.31 (s, 6 H, aryl−*Me*), 6.86 (s, 2 H, aryl of diphenyl), 7.54 (s, 2 H, aryl of diphenol), 6.90−7.4 (m, 5 H, phenyl); ^{13}C NMR −4.4, 16.0, 20.9, 121.2−145.45; ^{29}Si NMR −22.1.

{[Oxythiobis(4,6-dimethyl-*o*-phenylene)]dioxy}diphenylsilane, $OS(Me_2C_6H_2O)_2SiPh_2$ (3). The procedure was similar to the synthesis of **1**. The quantities used were as follows: **4** (1.4 g, 4.8 mmol), triethylamine (1.40 mL, 10.1 mmol), and Ph_2SiCl_2 (1.0 mL, 4.8 mmol): mp 231−235 °C (yield 1.5 g, 66%). ^{1}H NMR: 1.79 (s, 6 H, aryl−*Me*), 2.34 (s, 6 H, aryl−*Me*), 6.8−8.1 (m, 14 H, aryl). ^{13}C NMR: 15.93, 20.93, 121.16−136.0. ^{29}Si NMR: −38.0.

X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite-

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Table 1. Crystallographic Data for Compounds 1−4

	1	2A	2B	3	4
formula	$C_{18}H_{22}O_3SSi$	$C_{23}H_{24}O_3SSi$	$C_{23}H_{24}O_3SSi$	$C_{28}H_{26}OSSi$	$C_{16}H_{18}O_3S$
fw	346.51	408.57	408.57	470.64	290.36
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	Cc (No. 9)	$P2_1/n$ (No. 14)
cryst size (mm)	0.45 × 0.55 × 0.62	0.25 × 0.30 × 0.60	0.15 × 0.17 × 0.50	0.55 × 0.60 × 0.65	0.17 × 0.25 × 0.90
a (Å)	7.821(1)	9.071(2)	11.482(5)	15.607(5)	12.399(2)
b (Å)	9.115(2)	9.149(2)	15.426(5)	9.303(2)	9.606(2)
c (Å)	13.028(1)	13.343(3)	12.253(2)	34.560(3)	12.616(3)
α (deg)	90.56(1)	102.81(2)			
β (deg)	100.34(1)	95.57(2)	90.09(3)[a]	103.12(2)	101.92(2)
γ (deg)	92.04(1)	94.86(2)			
V (Å^3)	913.0(3)	1068.2(4)	2170.3(12)	4887(2)	1470.2(5)
Z	2	2	4	8	4
D_{calcd} (g/cm^3)	1.260	1.270	1.250	1.279	1.312
$\mu_{Mo\ K\alpha}$ (cm^{-1})	2.54	2.28	2.25	2.09	2.24
total no of rflns	2079	2444	2465	2945	1667
no. of rflns with $I > 2\sigma_I$	1854	2016	1292	2689	1273
R[b]	0.0358	0.0370	0.0609	0.0366[d]	0.0565
R_w[c]	0.0983	0.0997	0.1364	0.0928[d]	0.1492

[a] The space group of **2B** was uniquely determined as $P2_1/n$ by the systematic absences and further confirmed by the observed $2/m$, rather than mmm, diffraction symmetry. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$. [d] These values are for the configuration having the lowest R_w value.

monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Details of the experimental procedures have been described previously.[22]

The colorless crystals were mounted in thin-walled glass capillaries, which were sealed to protect the crystals from atmosphere as a precaution. Data were collected using the θ−2θ scan mode with 3° ≤ $2\theta_{Mo\ K\bar{\alpha}}$ ≤ 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[23] and SHELXL-93 for refinement.[24] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as isotropic scatters 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 2−6 for **1**−**4**, respectively. All figures are SNOOPI plots with thermal ellipsoids at the 50% probability level.

Syntheses. The new diol **4** was prepared in 85% yield by an oxidation reaction of 2,2′-thiobis(4,6-dimethylphenol) (**5**) with hydrogen peroxide in glacial acetic acid. This diol was then used to prepare **1**−**3** by a condensation reaction with the appropriate diorganodichlorosilane in CH_2Cl_2 solution in the presence of Et_3N. Yields ranged from 66 to 77%. The method is shown for **1** (eq 1). For silane **2**, two isomers were obtained, **2A** and **2B**, in a 2:1 ratio on ether extraction of the solid recrystallized from a hexane−dichloromethane solution. Isomer **2A** was present in the ether extract and isomer **2B** in the remaining globular polycrystalline solid. Both isomers were obtained in sufficient quantities by hand-picking for ^{1}H, ^{13}C, and ^{29}Si NMR as well as for the X-ray crystallographic studies.

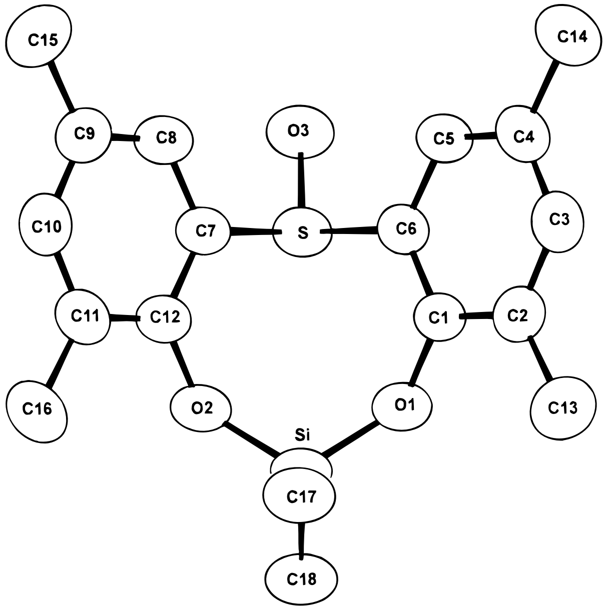
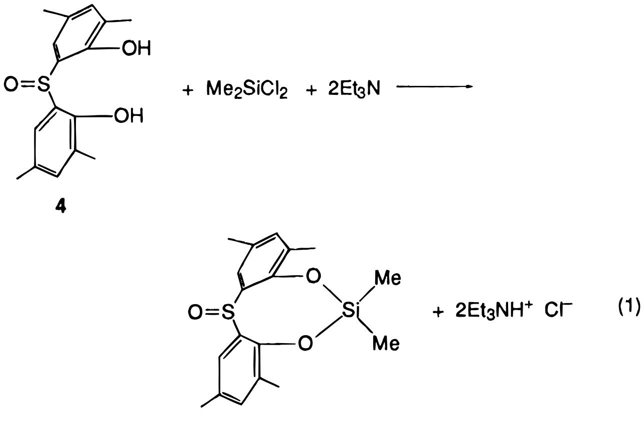


Figure 1. Molecular geometry and atom-labeling scheme for $OS(Me_2C_6H_2O)_2SiMe_2$ (**1**), with hydrogen atoms omitted for clarity.



4

1

(1)

All of the compounds **1**−**4** begin to decompose above

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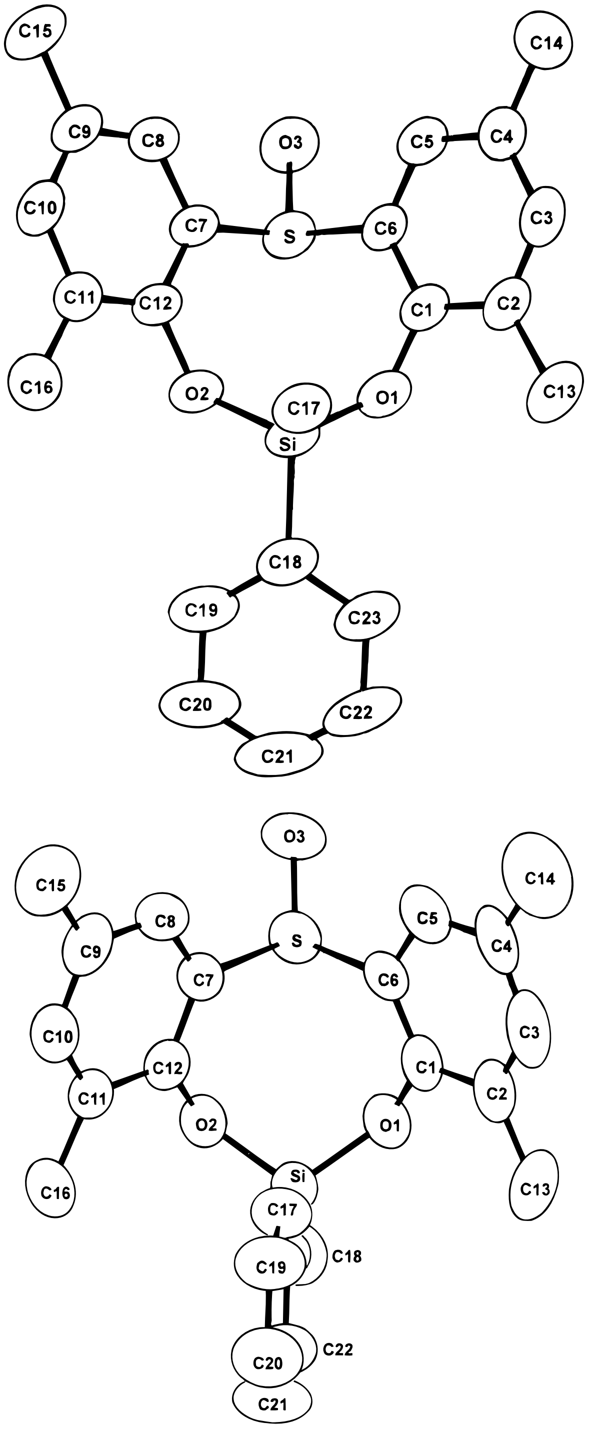

Figure 2. Molecular geometry and atom-labeling scheme, with hydrogen atoms omitted for clarity, for (a, top) $OS(Me_2C_6H_2O)_2Si(Me)Ph$ (**2A**) and (b, bottom) $OS(Me_2C_6H_2O)_2Si(Me)Ph$ (**2B**).

180 °C. However, they are quite stable to hydrolysis. A $CDCl_3$ solution of **1** with added water did not show any detectable change in the proton NMR spectrum even after 5 days at 25 °C.

Basic Structures. The X-ray studies of **1**−**3** confirm the lack of additional coordination from either the sulfur or oxygen atoms of the sulfoxide group (Figures 1−3). The eight-membered-ring arrangements for all three silanes are similar. The rings occupy a chairlike *anti* conformation where the oxygen atoms are further removed from silicon than the sulfur atoms. This feature is illustrated in Figure 5 for **2A** and **2B** as representative members of this series and shown independently in Figure 6 for the isolated ring arrangement in **2A**. The Si−S distances are slightly shorter than the van der Waals sum of 3.90 Å.[5] These are 3.615(1) Å (**1**), 3.618(1) Å (**2A**), 3.645(3) Å (**2B**), 3.633(2) Å (**3**), and

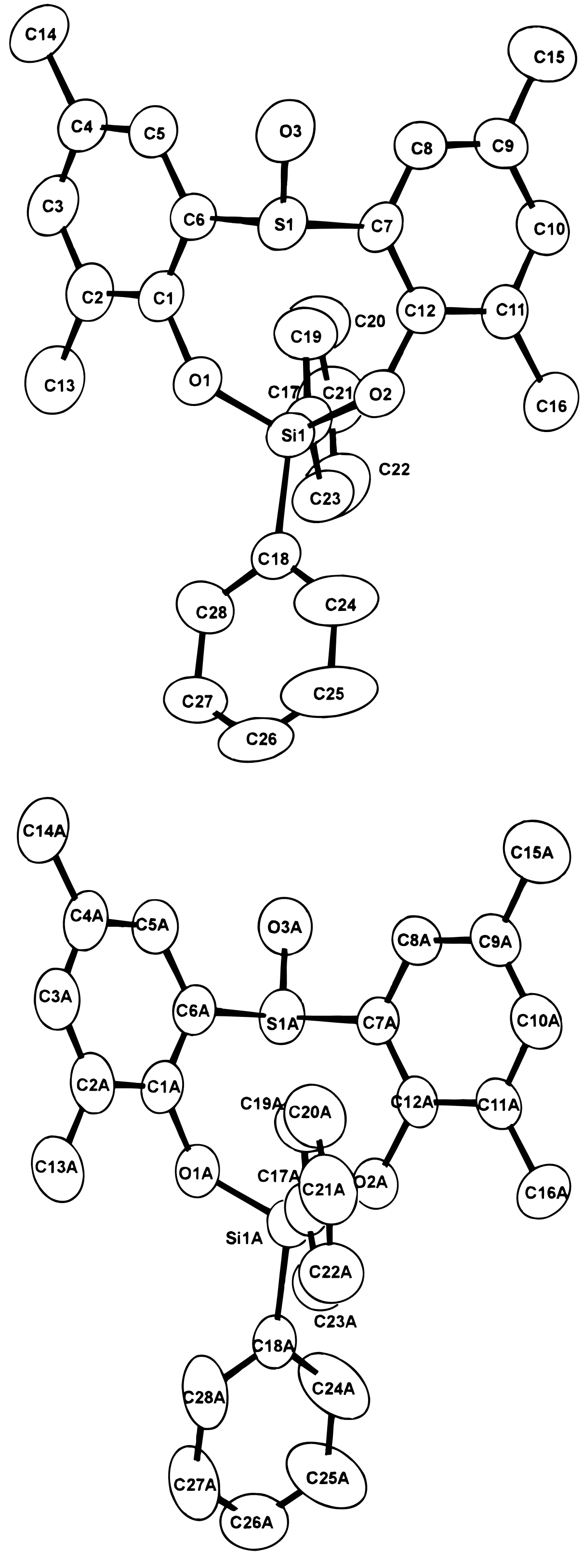

Figure 3. Molecular geometry and atom-labeling scheme for $OS(Me_2C_6H_2O)_2SiPh_2$ (**3**) with hydrogen atoms omitted for clarity: (a, top) view of the independent molecule containing Si(1) (b, bottom) view of the independent molecule containing Si(1A).

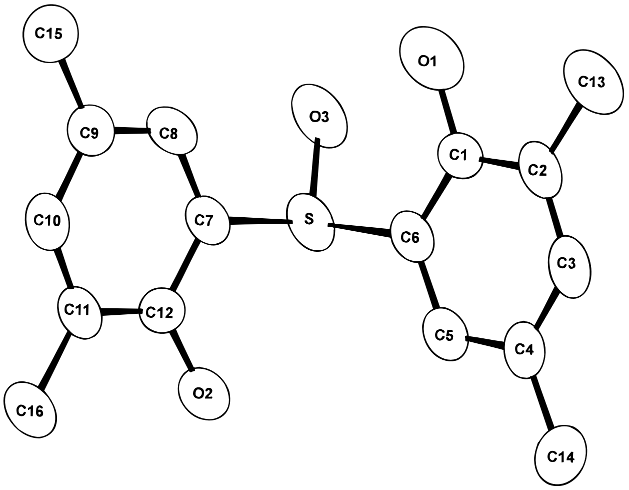

Figure 4. Molecular geometry and atom-labeling scheme for $OS(Me_2C_6H_2OH)_2$ (**4**), with hydrogen atoms omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $OS(Me_2C_6H_hO)_2SiMe_2$ (1)[a]

S−C(6)	1.800(3)	Si−C(17)	1.837(3)
S−C(7)	1.805(3)	O(1)−C(1)	1.382(3)
Si−O(1)	1.644(2)	O(2)−C(12)	1.380(3)
Si−O(2)	1.645(2)	C(1)−C(6)	1.384(4)
Si−C(18)	1.834(3)	C(7)−C(12)	1.386(4)
O(3)−S−C(6)	106.33(12)	C(12)−O(2)−Si	131.0(2)
O(3)−S−C(7)	105.33(12)	O(1)−C(1)−C(6)	119.5(2)
C(6)−S−C(7)	96.29(12)	O(1)−C(1)−C(2)	120.4(2)
O(1)−Si−O(2)	110.43(10)	C(1)−C(6)−S	120.4(2)
O(1)−Si−C(18)	105.73(14)	C(5)−C(6)−S	118.7(2)
O(2)−Si−C(18)	104.84(14)	C(8)−C(7)−S	118.5(2)
O(1)−Si−C(17)	110.02(14)	C(12)−C(7)−S	120.6(2)
O(2)−Si−C(17)	109.49(14)	O(2)−C(12)−C(7)	119.3(3)
C(18)−Si−C(17)	116.1(2)	O(2)−C(12)−C(11)	120.6(2)
C(1)−O(1)−Si	132.7(2)		

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

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $OS(Me_2C_6H_2O)_2Si(Me)Ph$ (2A)[a]

S−O(3)	1.487(2)	Si−C(17)	1.846(3)
S−C(6)	1.805(3)	O(1)−C(1)	1.390(4)
S−C(7)	1.796(3)	O(2)−C(12)	1.382(3)
Si−O(2)	1.648(2)	C(1)−C(6)	1.380(4)
Si−O(1)	1.649(2)	C(7)−C(12)	1.392(4)
Si−C(18)	1.836(3)		
O(3)−S−C(6)	105.95(13)	C(1)−O(1)−Si	122.9(2)
O(3)−S−C(7)	105.11(13)	C(12)−O(2)−Si	128.7(2)
C(7)−S−C(6)	98.00(13)	C(6)−C(1)−O(1)	119.8(3)
O(2)−Si−O(1)	109.68(11)	C(1)−C(6)−S	119.9(2)
O(2)−Si−C(18)	105.68(13)	C(5)−C(6)−S	119.3(2)
O(1)−Si−C(18)	106.54(13)	C(8)−C(7)−S	118.4(2)
O(2)−Si−C(17)	110.71(13)	C(12)−C(7)−S	121.3(2)
O(1)−Si−C(17)	110.07(14)	O(2)−C(12)−C(7)	119.8(3)
C(18)−Si−C(17)	113.96(14)		

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 2A.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for $OS(Me_2C_6H_2O)_2Si(Me)Ph$ (2B)[a]

S−O(3)	1.479(5)	Si−C(17)	1.838(7)
S−C(6)	1.783(8)	O(1)−C(1)	1.393(8)
S−C(7)	1.810(7)	O(2)−C(12)	1.376(8)
Si−O(2)	1.646(5)	C(1)−C(2)	1.371(10)
Si−O(1)	1.652(5)	C(7)−C(12)	1.390(9)
Si−C(18)	1.815(8)		
O(3)−S−C(6)	106.5(4)	C(1)−O(1)−Si	129.7(4)
O(3)−S−C(7)	104.9(3)	C(12)−O(2)−Si	127.7(4)
C(6)−S−C(7)	97.8(3)	C(6)−C(1)−O(1)	118.2(6)
O(2)−Si−O(1)	108.7(3)	C(1)−C(6)−S	122.3(6)
O(2)−Si−C(18)	106.2(3)	C(5)−C(6)−S	119.0(6)
O(1)−Si−C(18)	105.8(3)	C(8)−C(7)−S	118.7(6)
O(2)−Si−C(17)	109.3(3)	C(12)−C(7)−S	119.4(6)
O(1)−Si−C(17)	111.2(3)	O(2)−C(12)−C(7)	120.3(6)
C(18)−Si−C(17)	115.3(4)		

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 2B.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for $OS(Me_2C_6H_2O)_2SiPh_2$ (3)[a]

S(1)−O(3)	1.487(5)	S(1A)−O(3A)	1.485(5)
S(1)−C(6)	1.799(6)	S(1A)−C(6A)	1.790(6)
S(1)−C(7)	1.805(6)	S(1A)−C(7A)	1.811(6)
Si(1)−O(1)	1.628(4)	Si(1A)−O(1A)	1.634(4)
Si(1)−O(2)	1.655(4)	Si(1A)−O(2A)	1.648(4)
Si(1)−C(18)	1.837(6)	Si(1A)−C(18A)	1.840(6)
Si(1)−C(17)	1.851(6)	Si(1A)−C(17A)	1.859(6)
O(1)−C(1)	1.388(7)	O(1A)−C(1A)	1.390(7)
O(2)−C(12)	1.397(7)	O(2A)−C(12A)	1.407(7)
C(1)−C(6)	1.378(8)	C(1A)−C(6A)	1.374(8)
C(7)−C(12)	1.389(8)	C(7A)−C(12A)	1.378(8)
O(3)−S(1)−C(6)	105.7(3)	O(3A)−S(1A)−C(6A)	105.6(3)
O(3)−S(1)−C(7)	105.5(3)	O(3A)−S(1A)−C(7A)	105.6(3)
C(6)−S(1)−C(7)	98.5(3)	C(6A)−S(1A)−C(7A)	98.8(3)
O(1)−Si(1)−O(2)	108.7(2)	O(1A)−Si(1A)−O(2A)	109.1(2)
O(1)−Si(1)−C(18)	106.7(3)	O(1A)−Si(1A)−C(18A)	106.6(3)
O(2)−Si(1)−C(18)	106.9(3)	O(2A)−Si(1A)−C(18A)	106.6(3)
O(1)−Si(1)−C(17)	110.5(3)	O(1A)−Si(1A)−C(17A)	110.1(3)
O(2)−Si(1)−C(17)	110.9(2)	O(2A)−Si(1A)−C(17A)	111.1(2)
C(18)−Si(1)−C(17)	112.9(3)	C(18A)−Si(1A)−C(17A)	113.2(3)
C(1)−O(1)−Si(1)	131.7(4)	C(1A)−O(1A)−Si(1A)	131.6(4)
C(12)−O(2)−Si(1)	121.3(4)	C(12A)−O(2A)−Si(1A)	121.1(4)
C(6)−C(1)−O(1)	119.8(5)	C(6A)−C(1A)−O(1A)	119.7(5)
C(1)−C(6)−S(1)	119.9(5)	C(1A)−C(6A)−S(1A)	120.5(5)
C(12)−C(7)−S(1)	121.2(4)	C(12A)−C(7A)−S(1A)	121.3(4)
C(7)−C(12)−O(2)	119.9(5)	C(7A)−C(12A)−O(2A)	119.8(5)

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

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for $OS(Me_2C_6H_2OH)_2$ (4)[a]

S−O(3)	1.519(4)	O(2)−C(12)	1.361(6)
S−C(6)	1.781(5)	C(1)−C(6)	1.383(7)
S−C(7)	1.785(5)	C(7)−C(12)	1.382(6)
O(1)−C(1)	1.374(6)		
O(3)−S−C(6)	105.9(2)	C(5)−C(6)−S	117.2(4)
O(3)−S−C(7)	105.8(2)	C(12)−C(7)−C(8)	120.7(5)
C(6)−S−C(7)	100.0(2)	C(12)−C(7)−S	117.9(4)
O(1)−C(1)−C(2)	117.0(5)	C(8)−C(7)−S	121.4(4)
O(1)−C(1)−C(6)	122.4(5)	O(2)−C(12)−C(7)	115.9(4)
C(1)−C(6)−C(5)	120.2(5)	O(2)−C(12)−C(11)	124.0(4)
C(1)−C(6)−S	122.5(4)	C(7)−C(12)−C(11)	120.1(4)

[a] Numbers in parentheses are estimated standard deviations. Atoms are labeled to agree with Figure 4.

3.628(2) Å (**3**). There are two independent molecules per unit cell for **3**. The corresponding Si−O distances are much longer than the sum of the van der Waals radii of 3.60 Å.[5] They are 5.102(2) Å (**1**), 5.095(2) Å (**2A**), 5.121(6) Å (**2B**), 5.114(5) Å (**3**), and 5.108(5) Å (**3**).

In the structure of the diphenol **4**, one sees in Figure 4 that the OH groups are pointing in opposite directions, suggesting that rotation about the C−S bond is relatively free since the *cis* orientation is required on formation of **1**−**3**.

Structural Comparisons. It is interesting that there is little change in any of the chemical shifts in the solution-state ^1H NMR spectra of **1** between 23 and 95 °C obtained in $C_6D_5CD_3$. The presence of two methyl signals is consistent with the solid-state structure

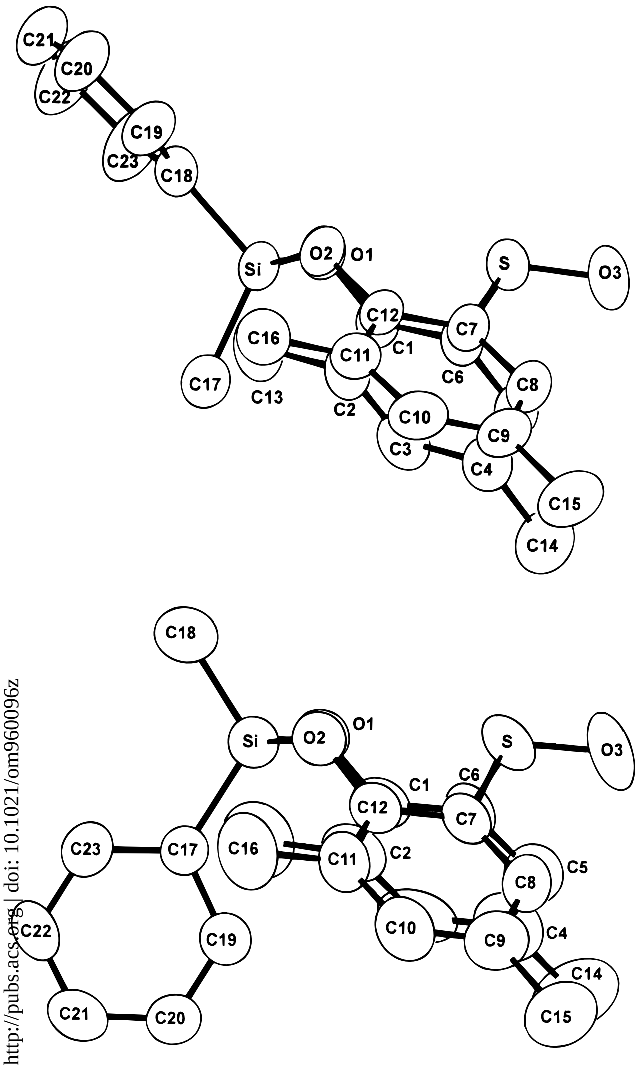

Figure 5. SNOOPI diagrams showing alternative views emphasizing the conformation of the eight-membered ring in relation to the rest of the molecule for (a, top) **2A** and (b, bottom) **2B**.

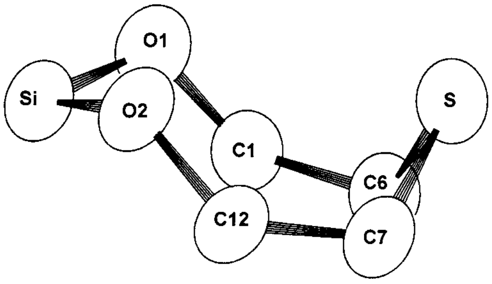

Figure 6. SNOOPI diagram showing the conformation of the eight-membered ring in **2A** isolated from the rest of the molecule.

shown in Figure 1. The temperature invariance suggests the lack of any ring pseudorotation of the type shown in Figure 7, and hence, the presence of a rigid conformation is indicated. On comparison with the methyl signals for the isomers **2A** and **2B**, we may assign the more shielded methyl signal for **1** at 0.60 ppm to the one that is oriented *cis* to the sulfoxide group. In **2B**, having a similar *cis* orientation, the methyl signal is at 0.90 ppm in the same solvent, $CDCl_3$. Likewise, the methyl resonance at 0.02 ppm for **1** is assignable to the methyl group that is oriented *trans* to the sulfoxide group. This signal is close to that for the methyl resonance in **2A**, which has a similar *trans* orientation, at 0.24 ppm in the same $CDCl_3$ solvent.

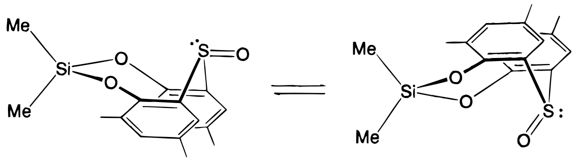

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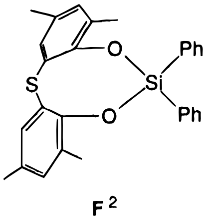
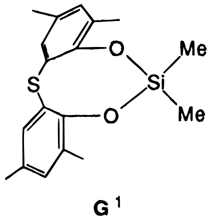
Figure 7. Absence of rapid ring pseudorotation, indicated by the temperature invariance of the two methyl silicon signals observed in the proton NMR spectrum.

The ^{29}Si chemical shift for **3** of −38.0 ppm in $CDCl_3$ is almost identical with that for the similarly constituted diphenylsilane **F**[2] (−38.4 ppm in $CDCl_3$), which contains a sulfur atom in place of the sulfoxide group. Both of these cyclic silanes lack any donor atom coordination and have the same type of structure with the rings in *anti* chair conformations. For **F**, the Si−S distance is 3.630(2) Å, about the same as that for the two independent molecules of **3**, 3.633(2) and 3.628(2) Å.



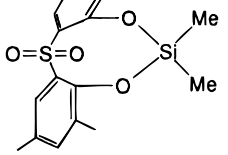
F [2]



G [1]

Further, we can make a comparison between the ^{29}Si chemical shifts of the related cyclic silanes **1** and **G**.[1] Silane **1** lacks donor atom coordination, while **G** has sulfur donor coordination promoting silicon toward a trigonal-bipyramidal geometry with an average Si−S distance of 3.286(1) Å. There are two independent molecules per unit cell for **G**. Consistent with the degree of pentacoordination for **G**, ∼36% from a tetrahedron toward a TBP, the ^{29}Si chemical shift is further upfield, −13.22 ppm, compared to that for **1**, −4.5 ppm, lacking any significant coordination. Both spectra are recorded in $CDCl_3$ solution.

It is noted that, only when the eight-membered-ring system containing either sulfur[1,2] or sulfoxide has methyl substituents on the aryl groups, donor action is not always observed, *e.g.*, for silanes **1** and **F**.[2] However, **G**,[1] which differs from **F** in the acyclic substituent makeup, does exhibit sulfur donor action. In the following paper[25] concerning eight-membered rings with SO_2 groups in place of the SO group, the same holds true. Silane **H**[25] is found to lack Si−O donor action compared to other members of this series studied that have increased alkyl substitution.



H [25]

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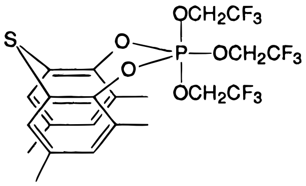
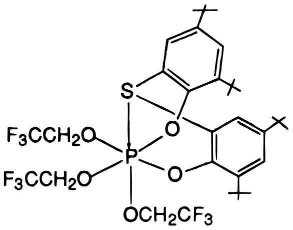
(25) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Organometallics* **1996**, *15*, 3189.

We can make this same comparison in phosphorus chemistry, where the monocyclic pentaoxyphosphorane **I**[26] is the only member of a more extensive series,[26−30] *e.g.*, **J**,[26] that lacks P−S donor action leading to hexacoordination. In this case, the ring system of **I** is in a chairlike conformation with the phosphorus and sulfur atoms in an *anti* ring arrangement. This results in a P−S distance of 3.504(3) Å, not too far from the van der Waals sum of 3.75 Å.[5] Other members having increased alkylation of the aryl ring components have boatlike ring conformations with the phosphorus and sulfur atoms in a *syn* arrangement.[26−30] This gives a series of geometries ranging from 44% to 71% along a coordinate toward an octahedron from a square pyramid.[27]



P–S = 3.504(3)Å

I[26]



P–S = 2.504(3)Å

J[26]

Conclusion

In a series of diorganosilanes containing an eight-membered ring with a bridging sulfinyl group, additional coordination at silicon by the latter group is precluded by the preference for chairlike ring conformations. The preference seems to be associated with the location of methyl substituents, which have low steric requirements on aryl groups present as ring components. Comparison with pentaoxyphosphorane geometries shows a similar relation regarding donor coordination with this same type of ring system containing a sulfur atom in place of the SO group.

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged.

Supporting Information Available: Atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for **1** (Tables S1−S4), **2A** (Tables S5−S8), **2B** (Tables S9−S12), **3** (Tables S13−S16), and **4** (Tables S17−S20) (23 pages). Ordering information is given on any current masthead page.

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