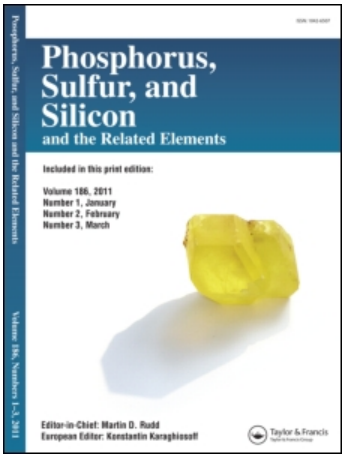

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CYCLIC SILANES. SULFUR-INDUCED PENTACOORDINATION IN A DISILOXANE

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CYCLIC SILANES. SULFUR-INDUCED PENTACOORDINATION IN A DISILOXANE[1,2]

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Reactions of chlorosilanes with diols capable of forming eight-membered-ring systems led to new cyclic silanes. With tetramethylenedichlorosilane ($(CH_2)_4SiCl_2$) and $S[(t\text{-}Bu)_2C_6H_2OH]_2$, the bicyclic silane $S[(t\text{-}Bu)_2C_6H_2O]_2Si(CH_2)_4$ (**2**) was obtained in 89% yield, whereas with $SiCl_4$, a hydrolysis reaction dominated, yielding the cyclic disiloxane $\{S[(t\text{-}Bu)_2C_6H_2O]_2Si(OCH_2CF_3)\}_2O$ (**1**) in 62% yield. A similar reaction with a related diol having a methylene group in place of sulfur gave $CH_2[(t\text{-}Bu)MeC_6H_2O]_2Si(CH_2)_4$ (**3**). X-ray studies of **1** and **3** are reported, as well as NMR spectral data on all three new cyclic silicon compounds. Structural parameters of **1** indicate silicon–sulfur interactions with the geometry at the silicon atoms displaced about halfway from a tetrahedron toward a trigonal bipyramid. The upfield ^{29}Si chemical shift for **1** in the solid state is shown to be in the pentacoordinate region and thus confirms the presence of a sulfur–silicon donor interaction. The rings of both **1** and **3** have boat or tublike conformations. Comparison of ring distortions of the cyclic silicon compounds with analogous ring geometries at related cyclic phosphoranes indicates that decreasing ring distortion parallels decreasing central atom–sulfur distance, leading to increased coordination. Disiloxane **1** crystallizes in the monoclinic space group $P2_1/n$ with a = 10.490(3) Å, b = 25.599(2) Å, c = 24.089(3) Å, β = 96.64(1)°, and Z = 4. Silane **3** crystallizes in the triclinic space group $P\bar{1}$ with a = 10.149(4) Å, b = 10.586(4) Å, c = 12.392(3) Å, α = 104.65(3)°, β = 94.81(2)°, γ = 102.52(3)°, and Z = 2. The final conventional unweighted residuals are 0.159 (**1**) and 0.057 (**3**).

INTRODUCTION

In our earlier work with silicon compounds, we were concerned with ring conformational preferences and site occupancy for anionic cyclic silicates assuming square-pyramidal and trigonal-bipyramidal structures.[3] These studies extended over ring sizes from five- to seven-membered[3,4] and resulted in the formation of the first five-coordinated anionic silicates with six- and seven-membered oxygen-containing rings (**A**–**C**).[5] The latter were all isolated as K^+, 18-crown-6-salts.

In companion work with phosphorus compounds,[6,7] we recently extended our studies to pentaoxyphosphoranes with sulfur-containing eight-membered rings.[1b,8–12] A series of these compounds formed showing varying degrees of sulfur coordination

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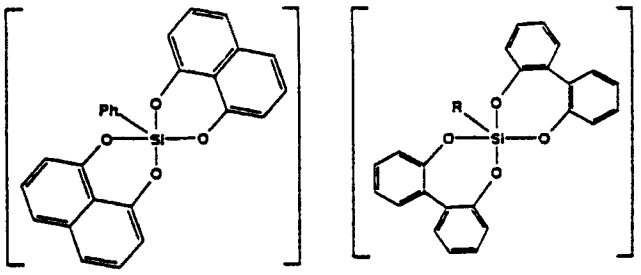
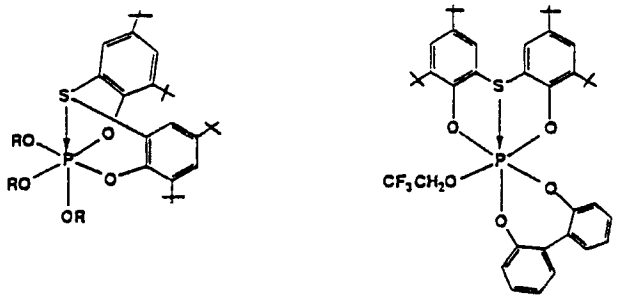


A B (R = O-*t*-Bu) C (R = F)

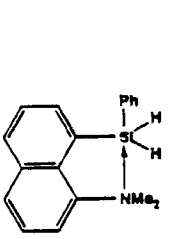
to phosphorus, resulting in structural displacements from square pyramidal to octahedral, as found from X-ray studies.[8–10,12] The range along this displacement coordinate toward hexacoordination for six compounds varied from 44% to 71%,[12] the variation being attributable to changing electronic requirements of ring substituents and acyclic ligands.[10] Representative members are **D**–**F**,[8–10] having a constant ring component but different ligands varying in electron-withdrawing ability in the order $(OC_6H_4)_2 > OCH_2CF_3 > OPh$.[10] The respective displacements, SP → O_h, are 60.8%, 64.5%, and 70.8%.[12]

It is of interest to investigate the structural consequences of the presence of this type of eight-membered ring in a silicon atom environment and to learn whether the tendency for sulfur coordination is comparable with that observed in the phos-

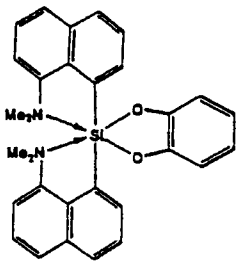


D[10] (R = OPh) E[8] (R = OCH_2CF_3) F[9]

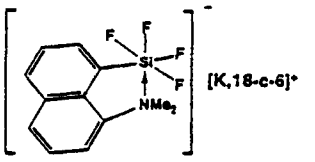
phorus series. It is known, particularly from the work of Corriu and co-workers,[13] that pendant donor nitrogen atoms increase the coordination at silicon through intramolecular ring closure, e.g., formation of **G**[14] and **H**[15] as neutral entities and **I**[16] as an anionic complex. In these examples, there is appreciable shortening of the Si–N distances from the van der Waals sum. In **I**, the Si–N distance is 2.21 Å. This compares with the value for the covalent Si–N bond length of 1.93 Å.[17] However, in **H** and several related structures, the Si–N distances fall in the range of 2.50–2.81 Å and the geometry at silicon remains largely tetrahedral. In consideration of sulfur at silicon in place of nitrogen, donor coordination is a likely possibility.



G[14]



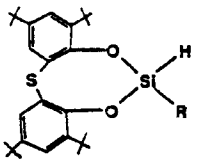
H[15]



I[16]

Like pentacoordinate phosphorus,[18] both the phosphorus and silicon species which have achieved increased coordination due to donor atom interactions serve as models for intermediates in nucleophilic substitution reactions.[3,13] In addition, many of these compounds exhibit enhanced reactivity due to the accompanying weakening of reactive bonds.[3,13] In the case of the sulfur-induced hexacoordination appearing in the phosphorus series, rapid hydrolysis is postulated to take place via these forms, leading to cyclic or acyclic phosphates depending on the leaving ability of the group undergoing cleavage.[1b]

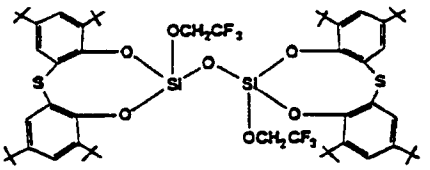
Previous work by Pastor and co-workers[19] led to the first dioxathiasilocin ring system formed (**J**) by the reaction of the alkylated thiobis(phenol) $S[(t\text{-}Bu)_2C_6H_2OH]_2$ with dichlorosilanes in the presence of Et_3N. To accomplish our objective of in-



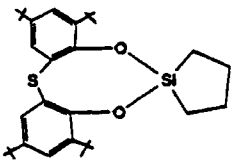
J[19] (R = Me, Ph)

ducing Si–S coordination leading to hypervalent cyclic silicon species, we followed the general synthetic route described above[19] in carrying out the reactions of $SiCl_4$ and tetramethylenedichlorosilane ($(CH_2)_4SiCl_2$) with the sulfur-bridging aromatic diol $S[(t\text{-}Bu)_2C_6H_2OH]_2$. For comparison, $(CH_2)_4SiCl_2$ was reacted with a similar diol, $CH_2[(t\text{-}Bu)MeC_6H_2OH]_2$, having a methylene group in place of the sulfur atom.

The formation of the expected cyclic silane in the reaction involving $SiCl_4$ was not attainable due to an ensuing hydrolysis process. However, this led to the most interesting aspect of our study in the isolation of the cyclic disiloxane product $\{S[(t\text{-}Bu)_2C_6H_2O]_2Si(OCH_2CF_3)\}_2O$ (**1**), possessing a Si–S interaction. Reactions of



1



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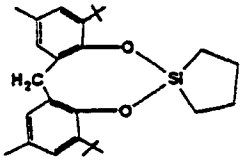


3

$(CH_2)_4SiCl_2$ yielded the desired bicyclic silanes $S[(t\text{-}Bu)_2C_6H_2O]_2Si(CH_2)_4$ (**4**) and $CH_2[(t\text{-}Bu)MeC_6H_2O]_2Si(CH_2)_4$ (**3**). The structures of **1** and **3** were obtained by X-ray analysis, while NMR measurements were performed on all three derivatives to assist in establishing structural preferences in solution and in the solid state.

EXPERIMENTAL

Chemicals were obtained from Aldrich, Fisher Scientific, Petrarch, or Fluka and used without further purification. Solvents were of HPLC grade (Fisher Scientific). Further purification was done according to standard procedures.[20]

^1H (299.9 MHz), ^{19}F (282.2 MHz), and ^{29}Si (59.59 MHz) NMR solution-state spectra were recorded on a Varian XL 300 FT-NMR spectrometer. ^{29}Si NMR spectra were obtained with the use of the INEPT program.[21] Solid-state ^{29}Si NMR spectra were recorded on a General Electric GN-300 NMR spectrometer, equipped with a multinuclear 7-mm MAS NMR probe from Doty Scientific. Spectra were acquired with the cross-polarization/magic angle spinning (CPMAS) technique, using contact times of 5–10 ms and relaxation delays of 10–20 s, at spinning speeds between 5 and 7 kHz. The Hartmann-Hahn condition was optimized using a sample of solid $[(CH_3)_3Si]_4Si$. ^1H and ^{29}Si chemical shifts are reported in ppm relative to tetramethylsilane (external). ^{19}F chemical shifts are reported relative to fluoro-trichloromethane (external). All NMR spectra were obtained at 23 °C, and shifts are reported in ppm.

Silicon tetrachloride and CF_3CH_2OH were purchased from Aldrich, and tetramethylenedichlorosilane was obtained from Petrarch Systems, Inc. 2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol)[22] and 2,2′-thiobis(4,6-di-*tert*-butylphenol)[19] were prepared by literature methods. Et_3N (Aldrich) was distilled over KOH pellets. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk-type glassware.[23]

Syntheses. 1,1:3,3-Bis{[thiobis(4,6-di-tert-butyl-o-phenylene)]dioxy}-1,3-bis(2,2,2-trifluoroethoxy)di-siloxane, $\{S[(t\text{-}Bu)_2C_6H_2O]_2Si(OCH_2CF_3)\}_2O$ (**1**). To a solution of tetrachlorosilane (2 mL, 2.96 g, 17.5 mmol) in 20 mL of toluene was added dropwise a solution of 2,2′-thiobis(4,6-di-*tert*-butylphenol) (7.72 g, 17.5 mmol) and Et_3N (5.10 mL, 3.70 g, 36.7 mmol) in 150 mL of Et_2O and 50 mL of toluene. The reaction flask was kept at 0–5 °C until the addition was complete and then gradually warmed to 25 °C. The solution was stirred at this temperature for 18 h. The reaction flask was cooled again to 0–5 °C, and to it was added a solution of 2,2,2-trifluoroethanol (1.27 mL, 1.75 g, 17.5 mmol) and Et_3N (5.10 mL, 3.70 g, 36.7 mmol) in 50 mL of Et_2O. Stirring was continued for 49 h followed by filtration to remove $Et_3NH^+Cl^-$. The filtrate was concentrated under reduced pressure and the white residue extracted with an Et_2O/*n*-hexane mixture (150 mL/50 mL). Evaporation of the solvents under a slow purge of dry nitrogen yielded **1** as white needlelike crystals: mp 220–223 °C (yield 6.2 g, 62%). ^1H NMR ($CDCl_3$): 1.24–1.40 (m, 72H, $C(CH_3)_3$), 4.15 (br, 4H, OCH_2CF_3), 7.25–7.45 (m, 8H, H (Ar)). ^{19}F NMR ($CDCl_3$): −77.17 (s). ^{29}Si NMR (solid state): −99.35, −107.84. Anal. Calcd for $C_{60}H_{84}F_6O_7S_2Si_2$: C, 62.59; H, 7.30. Found: C, 62.36; H, 7.32.

{[Thiobis(4,6-di-tert-butyl-o-phenylene)]dioxy}tetramethylenesilane, $S[(t\text{-}Bu)_2C_6H_2O]_2Si(CH_2)_4$ (**2**). Quantities used were as follows: tetramethylenedichlorosilane (3.09 mL, 3.66 g, 23.5 mmol), 2,2'-thiobis(4,6-di-*tert*-butylphenol) (10.42 g, 23.5 mmol), Et_3N (7.20 mL, 51.7 mmol), toluene (25 mL), and diethyl ether (150 mL). A procedure similar to the synthesis of 3 was followed. The reaction mixture was stirred at 25 °C for 40 h. The silane was crystallized from a CH_2Cl_2/MeCN mixture (50 mL/10 mL); mp 224 °C (yield 9.0 g, 89%). ^1H NMR ($CDCl_3$): 0.95 (m, 4H, Si–CH_2), 1.15 (m, 4H, CH_2), 1.28 (s, 18H, $C(CH_3)_3$), 1.36 (s, 18H, $C(CH_3)_3$), 7.26–7.55 (m, 4H, H (Ar)). ^{29}Si NMR ($CDCl_3$): −1.62. ^{29}Si NMR (solid state): −6.55. Anal. Calcd for $C_{32}H_{48}O_2SSi$: C, 73.26, H, 9.16. Found: C, 73.13; H, 9.27.

{[Methylenebis(4,6-di-tert-butyl-o-phenylene)]dioxy}-tetramethylenesilane, $CH_2[(t\text{-}Bu)MeC_6H_2O]_2Si(CH_2)_4$ (**3**). To a solution of tetramethylenedichlorosilane (3.09 mL, 3.66 g, 23.5 mmol) in 25 mL of toluene, kept at 0–5 °C, was added dropwise a mixture of 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol) (8.00 g, 23.5 mmol) and Et_3N (7.20 mL, 51.7 mmol) in 150 mL of toluene. The reaction mixture was stirred at 25 °C for 24 h. After 150 mL of Et_2O was added to the reaction flask, the solution was filtered, followed by removal of the solvents under reduced pressure. The white solid was crystallized from a solvent mixture of Et_2O and hexane (150 mL/50 mL); mp 173–174 °C (yield 9.4 g, 95%), ^1H NMR ($CDCl_3$): 0.95 (br, 4H, Si–CH_2), 1.15 (br, 4H, CH_2), 1.35 (s, 18H, $C(CH_3)_3$), 2.26 (s, 6H, CH_3), 3.45 (d, 1H, $^2J_{HH}$ = 14.7 Hz, bridging CH_2), 4.30 (d, 1H, $^2J_{HH}$ = 14.8 Hz, bridging CH_2), 6.95 (4H, H (Ar)). ^{29}Si NMR ($CDCl_3$): 5.44 (s). ^{29}Si NMR (solid state): 5.88. Anal. Calcd for $C_{27}H_{38}O_2Si$: C, 76.77; H, 9.00. Found: C, 76.58; H, 9.10.

X-ray Studies. All X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation. Details of the experimental procedures have been described previously.[24]

Crystals were mounted in thin-walled glass capillaries which were sealed as a precaution against moisture sensitivity. Data was collected using the θ–2θ scan mode. No corrections were made for absorption. The structures were solved by use of direct methods and difference Fourier techniques and were refined by full-matrix least squares.[25]

All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs. Crystallographic data are summarized in Table I.

X-ray Study for $\{S[(t\text{-}Bu)_2C_6H_2O]_2Si(OCH_2CF_3)\}_2O$ (**1**). Crystals of **1** grow as colorless clumps of laths and diffract poorly at higher angles. The crystal used for the study was cut to dimensions of 0.18 × 0.25 × 0.50 mm. A total of 6859 independent reflections was measured ($+h,+k,\pm l$; $3° \leq 2\theta_{Mo K\bar{\alpha}} \leq 42°$). One of the *t*-Bu groups (C21–C24) was poorly defined, and the trifluoroethyl group bound to oxygen O2 was so badly disordered that it was not possible to include the atoms of this group (F_3CCH_2) in the refinement. The Si, S, and O atoms were refined anisotropically. Hydrogen atoms, except for

TABLE I

Crystallographic Data for Compounds **1** and **3**

compd	**1**	**3**
formula	$C_{60}H_{84}O_7S_2F_6Si_2$	$C_{27}H_{38}O_2Si$
fw	1151.625	422.689
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	10.490(3)	10.149(4)
b, Å	25.599(2)	10.586(4)
c, Å	24.089(3)	12.392(3)
α, deg		104.65(3)
β, deg	96.64(1)	94.81(2)
γ, deg		102.52(3)
V, Å^3	6425(3)	1244(2)
Z	4	2
T, °C	23 ± 2	23 ± 2
λ, Å	0.710 73	0.710 73
D_{calc}, g cm^{-3}	1.195	1.129
μ, cm^{-1}	1.775	1.089
$R(F_o)^a$	0.159	0.057
$R_w(F_o)^a$	0.215	0.079

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

those of the poorly defined *t*-Bu group and those of the missing F_3CCH_2 group, were included as fixed isotropic scatterers in ideal positions. The final refinement was based on 2697 observed reflections ($I \geq 3\sigma_I$).

X-ray Study for $CH_2[(t\text{-}Bu)MeC_6H_2O]_2Si(CH_2)_4$ (**3**). The colorless crystal used for the study was cut from a large elongated parallelepiped and was an approximate triangular prism with edge lengths of 0.5 mm and a height of 0.25 mm. The crystal was only of moderate quality (broad peaks). A total of 2844 independent reflections was measured ($+h, \pm k, \pm l$; $3° \leq 2\theta_{Mo K\bar{\alpha}} \leq 43°$). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement as fixed isotropic scatterers (ideal positions or regularized difference Fourier positions for the two Me groups). The final refinement was based on 2026 observed reflections ($I \geq 3\sigma_I$).

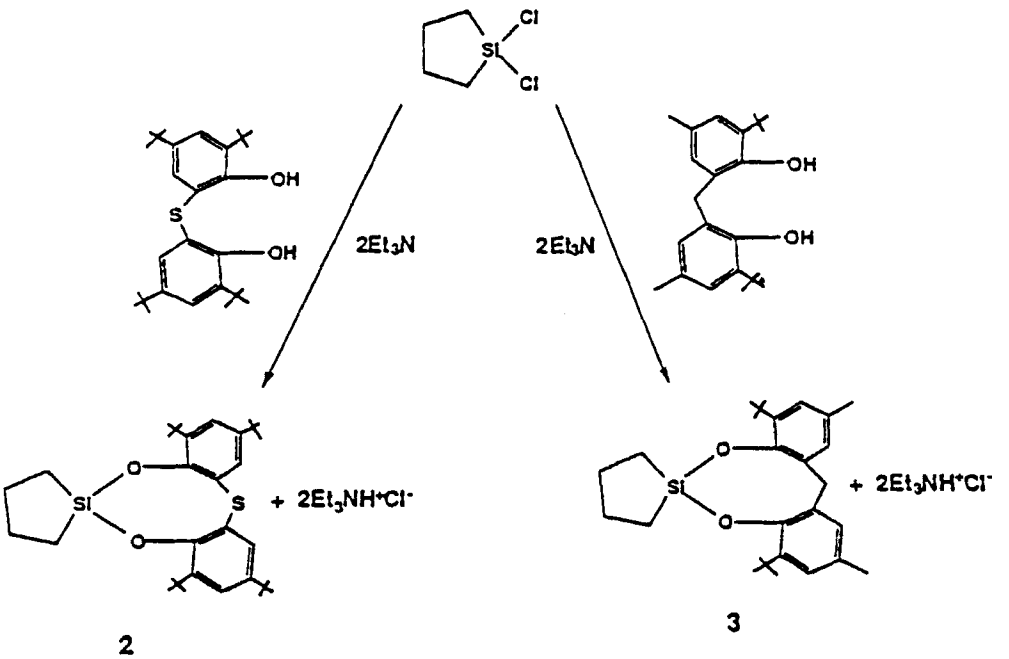
RESULTS AND DISCUSSION

Syntheses

The new cyclic silanes **2** and **3** are prepared in 89–95% yields by reacting tetramethylenedichlorosilane with the corresponding diols in the presence of Et_3N in toluene or toluene/ether solutions (Scheme 1).

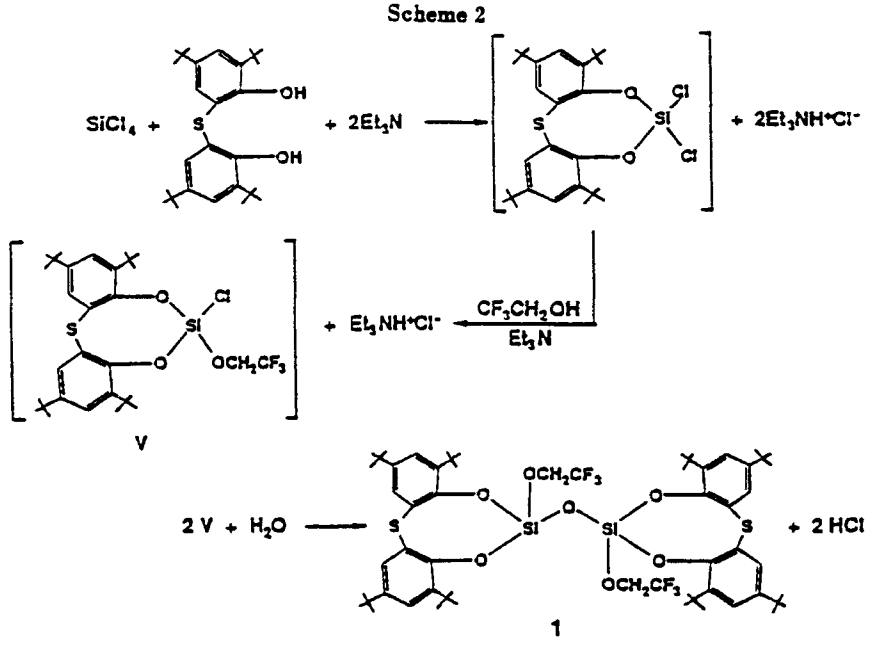
In the formation of the disiloxane **1**, the initial reaction described above was performed followed by treatment *in situ* with CF_3CH_2OH and additional Et_3N in an attempt to prepare **V**. However, hydrolysis ensued, no doubt due to the presence of reactive Si–Cl bonds in the proposed intermediates shown in Scheme 2. The disiloxane **1** was isolated in 62% yield.

Scheme 1



2 **3**

Scheme 2

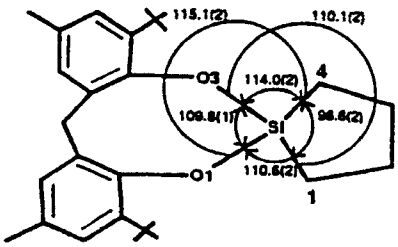


Basic Structures

Although not readily apparent in Figure 1, the geometries at the two silicon atoms of the cyclic disiloxane **1** are different. The expected tetrahedral orientation at each silicon is modified as described below by the nearness of the ring sulfur atoms, resulting in a tendency toward trigonal-bipyramidal formation. Each sulfur atom is positioned axially opposite a OCH_2CF_3 group. The structure of the cyclic silane **3** with a ring methylene group in place of a sulfur atom more nearly approaches the tetrahedral geometry.

Even considering the low refinement of **1**, the uncertainty in the silicon–sulfur bond distances are within the range for Si1–S1 of 3.01–3.07 Å and that for Si2–S2 of 3.08–3.14 Å based on the criterion that parameters within 3σ of each other are equal. These bond distance ranges provide a considerable measure of confidence in establishing a Si–S interaction, since the range of uncertainty is small (0.06 Å) compared to the difference between the van der Waals sum (3.90 Å)[26] and the sum of covalent radii (2.20 Å).[17]

This structural difference is made more clear by comparing the angles at silicon for **1** and **3**. Other than the angle at silicon for the five-membered ring of **3**, the



3

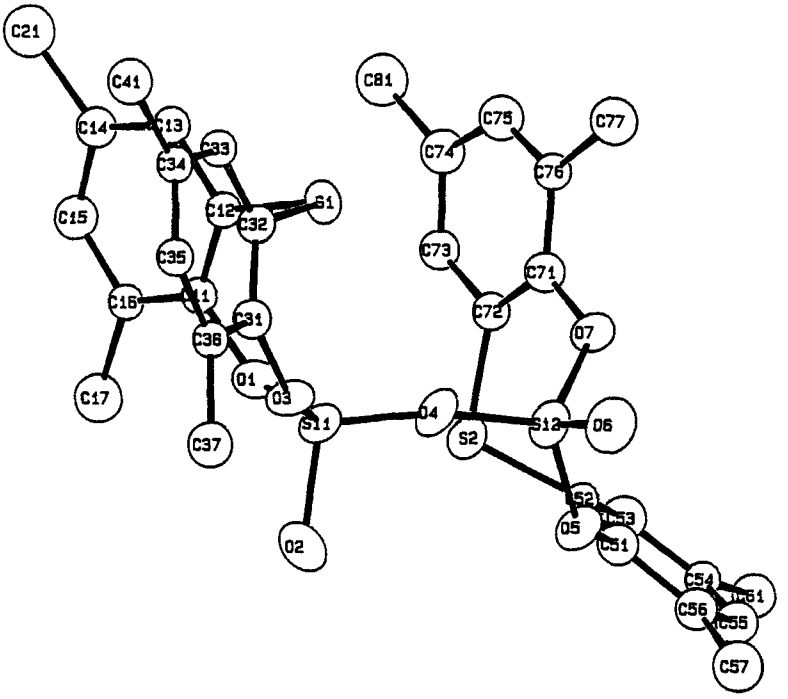
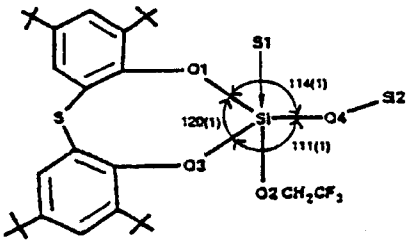


FIGURE 1 ORTEP plot of $\{S[(t\text{-Bu})_2C_6H_3O]_2Si(OCH_2CF_3)\}_2O$ (1) with thermal ellipsoids at the 30% probability level. Atoms of the F_3CCH_2 group, pendant atoms of the *t*-Bu groups, and all H atoms are omitted for clarity.

angles do not vary much from the tetrahedral value, whereas this is not the case for the cyclic disiloxane **1**. Here the eight-membered sulfur-containing ring opened up at silicon to 120(1)° compared to 109.8(1)° for this angle in **3**. This allows the sulfur atoms, which has a larger radius than carbon by 0.25 Å[17] (referring to the methylene group replacement from **3** to **1**), to be displaced toward the central silicon atom. The Si1–S1 distance in **1** is 3.04(1) Å, which compares with the Si–C nonbonding distance to the methylene carbon of **3** of 3.100(4) Å.



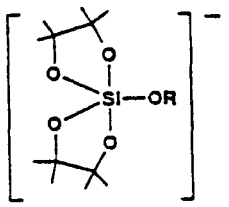
1 (Partial)

The structural displacement due to the sulfur interaction in **1** may be made more quantitative by noting how far the Si–S distance extends from the van der Waals sum of 3.90 Å[26] to the sum of covalent radii of 2.20 Å.[17] For Si1–S1, a displacement from the tetrahedron toward the trigonal bipyramid, $T_d \rightarrow$ TBP, is 53%. In a similar manner, by use of the sum of angles at silicon Si1 that constitute the trigonal

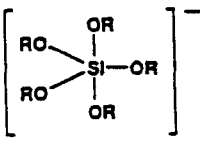
plane of the partially formed TBP in the schematic for **1** (345°) relative to the sum for a tetrahedron (328.40°) and a TBP (360°), a displacement $T_d \rightarrow$ TBP of 53% is computed. If we perform these same calculations for the silicon atom Si2 of the disiloxane **1**, we obtain a 47% displacement ($T_d \rightarrow$ TBP) from the Si2–S2 distance and 34% from the bond angles. For the cyclic silane **3**, this same type of calculation gives values of $T_d \rightarrow$ TBP of 36% (based on the Si–C22 distance) and 34% (based on the angles at silicon due to O3, O1, and C4 considered to constitute the incipient trigonal plane).

An average of the two values for each silicon atom gives $T_d \rightarrow$ TBP of 53% at Si1 and 41% at Si2 for **1** and 35% for **3**. It appears that a sulfur donor interaction at silicon Si1 of the disiloxane **1** is significant.

Examination of ^{29}Si NMR chemical shifts is useful in providing confirmational evidence that a sulfur–silicon interaction exists for **1**. Available ^{29}Si NMR data on six bicyclic anionic pentaoxysilicates of the type **Q**[27,28] show solution chemical shifts in the range from −109 to −112 ppm with an average of −111 ppm, whereas six acyclic anionic pentaoxysilicates represented by **S**[28] have solution ^{29}Si shifts in the range −127 to −144 ppm with an average value of −134 ppm. For bicyclic anionic derivatives **A**–**C**, having ring sizes larger than five, the solution ^{29}Si shifts, −132.4,



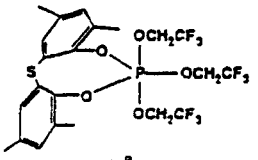
Q



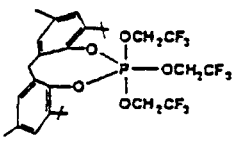
S

−125.8, and −125.5 ppm, respectively,[5] are closer to those observed for the acyclic anionic pentaoxysilicates. These trends with the number of rings and ring sizes in general are those found for ^{31}P NMR chemical shifts of the much more extensively studied oxyphosphorane compounds.[4]

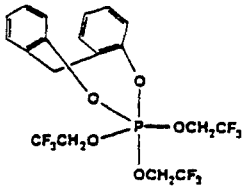
For analogous tetraoxy derivatives having the same sets of ligands as expressed by the pentaoxy silicates **S** (where R = Me. Et, *n*-Pr, *i*-Pr, CH_2CF_3, C_6H_4-Me-*p*),



N[8]



O[8,29]



P[8]

the solution-state ^{29}Si shifts[28] fall in the lower range, −79 to −100 ppm, with an average of −86 ppm. For the bicyclic tetracoordinate bis(pinacolate) $Si(O_2C_2Me_4)_2$, the solution chemical shift is −45.1 ppm.[28]

For the cyclic tetraoxy disiloxane **1**, ^{29}Si chemical shifts were observed in the solid-state NMR spectrum at −99.4 and −107.8 ppm, as expected for two crys-

TABLE II

Atomic Coordinates in Crystalline $\{S[(t\text{-}Bu)_2C_6H_2O]_2Si(OCH_2CF_3)\}_2O$ (**1**)[a]

atom[b]	*x*	*y*	*z*	atom[b]	*x*	*y*	*z*
S1	0.5275(8)	0.1333(4)	0.7650(4)	C37	0.858(3)	0.266(1)	0.872(1)
S2	0.3087(9)	,0.2434(4)	0.5937(4)	C38	0.915(4)	0.289(1)	0.823(2)
Si1	0.590(1)	0.2405(4)	0.7211(4)	C39	0.956(5)	0.271(2)	0.922(2)
Si2	0.297(1)	0.2735(4)	0.7184(4)	C40	0.747(4)	0.304(2)	0.884(2)
F4	0.246(4)	0.363(2)	0.865(2)	C41	0.859(4)	0.077(1)	0.937(2)
F5	0.430(4)	0.342(2)	0.905(2)	C42	0.800(5)	0.028(2)	0.927(2)
F6	0.408(5)	0.373(2)	0.827(2)	C43	0.855(5)	0.095(2)	0.995(2)
O1	0.617(2)	0.1981(9)	0.6733(9)	C44	0.992(5)	0.069(2)	0.933(2)
O2	0.644(2)	0.298(1)	0.695(1)	C51	0.192(3)	0.329(1)	0.630(1)
O3	0.667(2)	0.2356(8)	0.7838(9)	C52	0.185(3)	0.291(1)	0.590(1)
O4	0.440(2)	0.2521(9)	0.7243(9)	C53	0.104(4)	0.298(1)	0.542(1)
O5	0.273(2)	0.3247(9)	0.6787(9)	C54	0.022(3)	0.340(1)	0.533(1)
O6	0.268(2)	0.295(1)	0.7794(9)	C55	0.031(3)	0.376(1)	0.575(1)
O7	0.192(2)	0.2289(8)	0.7027(8)	C56	0.116(3)	0.374(1)	0.625(1)
C3	0.342(5)	0.290(2)	0.832(2)	C57	0.121(4)	0.419(2)	0.668(2)
C4	0.353(8)	0.350(3)	0.862(4)	C58	0.076(4)	0.399(2)	0.723(2)
C11	0.649(3)	0.145(1)	0.669(1)	C59	0.030(5)	0.465(2)	0.650(2)
C12	0.614(3)	0.112(1)	0.709(1)	C60	0.257(5)	0.440(2)	0.670(2)
C13	0.641(3)	0.058(1)	0.705(1)	C61	-0.077(3)	0.345(1)	0.480(1)
C14	0.708(3)	0.040(1)	0.665(1)	C62	–0.200(5)	0.324(2)	0.489(2)
C15	0.743(3)	0.077(1)	0.627(1)	C63	–0.034(5)	0.315(2)	0.434(2)
C16	0.716(3)	0.130(1)	0.629(1)	C64	–0.093(6)	0.400(2)	0.457(3)
C17	0.756(4)	0.167(2)	0.583(2)	C71	0.203(3)	0.184(1)	0.673(1)
C18	0.846(4)	0.210(2)	0.609(2)	C72	0.247(3)	0.186(1)	0.621(1)
C19	0.635(4)	0.191(2)	0.551(2)	C73	0.263(3)	0.140(1)	0.592(1)
C20	0.821(5)	0.136(2)	0.537(2)	C74	0.234(3)	0.093(1)	0.612(1)
C21	0.753(4)	–0.020(2)	0.664(2)	C75	0.188(3)	0.095(1)	0.667(2)
C22	0.672(7)	–0.057(3)	0.691(3)	C76	0.169(3)	0.137(1)	0.696(1)
C23	0.851(6)	–0.033(3)	0.636(3)	C77	0.115(4)	0.130(2)	0.752(2)
C24	0.645(8)	–0.041(3)	0.620(4)	C78	–0.021(4)	0.155(2)	0.748(2)
C31	0.712(3)	0.196(1)	0.821(1)	C79	0.192(4)	0.156(2)	0.801(2)
C32	0.662(3)	0.146(1)	0.816(1)	C80	0.098(7)	0.077(3)	0.774(3)
C33	0.709(3)	0.108(1)	0.855(1)	C81	0.255(4)	0.040(2)	0.580(2)
C34	0.805(3)	0.118(1)	0.896(1)	C82	0.376(5)	0.044(2)	0.553(2)
C35	0.846(3)	0.169(1)	0.900(1)	C83	0.280(5)	–0.005(2)	0.621(2)
C36	0.809(3)	0.210(1)	0.866(1)	C84	0.141(5)	0.033(2)	0.539(2)

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

TABLE III

Selected Distances (Å) and Angles (deg) for $\{S[(t\text{-}Bu)_2C_6H_2O]_2Si(OCH_2CF_3)\}_2O$ (1)[a]

Si1–S1	3.04(1)	Si2–S2	3.11(1)
S1–C12	1.79(3)	Si2–O5	1.62(2)
S1–C32	1.79(3)	Si2–O6	1.63(2)
S2–C52	1.78(3)	Si2–O7	1.60(2)
S2–C72	1.75(3)	O1–C11	1.40(4)
Si1–O1	1.63(2)	O3–C31	1.40(4)
Si1–O2	1.72(3)	O5–C51	1.38(4)
Si1–O3	1.63(2)	O6–C3	1.42(5)
Si1–O4	1.60(2)	O7–C71	1.37(4)
Si2–O4	1.59(2)		
Si1–S1–C12	83(1)	Si2–S2–C52	77(1)
Si1–S1–C32	84(1)	Si2–S2–C72	78(1)
C12–S1–C32	98(1)	O4–Si2–O7	113(1)
C52–S2–C72	107(2)	O5–Si2–O6	103(1)
O1–Si1–O2	103(1)	O5–Si2–O7	112(1)
O1–Si1–O3	120(1)	O6–Si2–O7	105(1)
O1–Si1–O4	114(1)	Si1–O1–C11	140(2)
O2–Si1–O3	105(1)	Si1–O3–C31	138(2)
O2–Si1–O4	103(1)	Si1–O4–Si2	168(2)
O3–Si1–O4	111(1)	Si2–O5–C51	127(2)
O4–Si2–O5	114(1)	Si2–O6–C3	130(3)
O4–Si2–O6	108(1)	Si2–O7–C71	129(2)

[a] Estimated standard deviations are given in parentheses. The atom-labeling scheme is shown in Figure 1.

TABLE IV

Atomic Coordinates in Crystalline $CH_2(t\text{-}BuMeC_6H_2O)_2Si(CH_2)_4$ (3)[a]

atom[b]	x	y	z
Si	0.3765(1)	0.2643(1)	0.14426(9)
O1	0.3373(2)	0.2820(2)	0.0197(2)
O3	0.2928(2)	0.3442(2)	0.2336(2)
C1	0.3368(4)	0.0828(4)	0.1398(4)
C2	0.4685(6)	0.0657(5)	0.1974(5)
C3	0.5896(5)	0.1648(6)	0.1825(6)
C4	0.5623(4)	0.3015(5)	0.1940(4)
C11	0.2667(3)	0.3671(3)	−0.0151(3)
C12	0.2999(4)	0.5033(4)	0.0437(3)
C13	0.2300(4)	0.5878(4)	0.0090(3)
C14	0.1283(4)	0.5408(4)	−0.0835(3)
C15	0.0979(4)	0.4052(4)	−0.1407(3)
C16	0.1640(4)	0.3147(3)	−0.1088(3)
C17	0.1232(4)	0.1643(4)	−0.1755(3)
C18	0.0055(5)	0.1333(5)	−0.2716(4)
C19	0.2479(5)	0.1263(5)	−0.2275(4)
C20	0.0751(5)	0.0765(4)	−0.0990(4)
C21	0.0554(5)	0.6334(4)	−0.1233(4)
C22	0.4118(4)	0.5629(4)	0.1453(3)
C31	0.3052(4)	0.4750(4)	0.2986(3)
C32	0.3581(4)	0.5817(4)	0.2566(3)
C33	0.3582(4)	0.7116(4)	0.3195(3)
C34	0.3071(4)	0.7332(4)	0.4204(4)

TABLE IV (*Continued*)

atom[b]	x	y	z
C35	0.2595(4)	0.6254(4)	0.4611(3)
C36	0.2567(4)	0.4921(4)	0.4031(3)
C37	0.2084(4)	0.3759(4)	0.4530(3)
C38	0.0832(5)	0.2719(4)	0.3775(4)
C39	0.1610(6)	0.4226(5)	0.5682(4)
C40	0.3254(5)	0.3082(5)	0.4702(4)
C41	0.3043(5)	0.8760(5)	0.4872(4)

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

TABLE V

Selected Distances (Å) and Angles (deg) in $CH_2(t\text{-}BuMeC_6H_2O)_2Si(CH_2)_4$ (3)[a]

Si–O1	1.628(3)	O3–C31	1.388(4)
Si–O3	1.630(3)	C1–C2	1.529(7)
Si–C1	1.862(4)	C2–C3	1.491(8)
Si–C4	1.857(4)	C3–C4	1.505(8)
O1–C11	1.390(5)	Si–C22	3.100(4)
O1–Si–O3	109.8(1)	Si–O1–C11	131.2(2)
O1–Si–C1	110.6(2)	Si–O3–C31	137.7(2)
O1–Si–C4	115.1(2)	Si–C1–C2	103.9(3)
O3–Si–C1	110.1(2)	C1–C2–C3	111.0(5)
O3–Si–C4	114.0(2)	C2–C3–C4	111.9(5)
C1–Si–C4	96.6(2)	Si–C4–C3	104.1(3)
C12–C22–C32	113.4(3)		

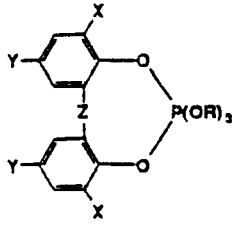
[a] Estimated standard deviations are given in parentheses. The atom-labeling scheme is shown in Figure 3.

tallographically independent silicon sites. This large upfield shift from the bicyclic bis(pinacolate) is viewed as an expression of pentacoordination due to the nearness of sulfur to silicon, as demonstrated by the X-ray crystallographic investigation. Since **1** has each silicon center coordinated as a monocyclic derivative, it is expected that the ^{29}Si shift in the absence of a silicon–sulfur interaction is intermediate between that for the bicyclic $Si(O_2C_2Me_4)_2$ and those expressed by the acyclic derivatives $Si(OR)_4$, namely between -45 and -86 ppm.[28] We associate the more upfield ^{29}Si chemical shift of -107.8 ppm with Si1 that is in a more pentacoordinate environment, 53% TBP, and the lower shift of -99.4 ppm with Si2 which is less pentacoordinated, 43% TBP (Table VI).

The possibility of a sulfur–silicon interaction for the cyclic silane **2**, which lacks an X-ray structure, is expected to be diminished relative to the disiloxane **1**. The presence of two Si–C bonds in **2** in place of Si–O bonds in **1** should increase the electron density at silicon and make it less receptive to sulfur donor action. For **2**, the ^{29}Si chemical shift is -1.62 ppm in solution and -6.55 ppm in the solid state. These values are close to that for **3**, which lacks a ring sulfur atom. Here the ^{29}Si shift is 5.44 ppm in solution and 5.88 ppm in the solid. It might be anticipated that if **2** had a significant sulfur–silicon interaction, the ^{29}Si shift might approach that of the related bicyclic anionic silicate **T**, which has a pentacoordinate structure.[4] The ^{29}Si shift for **T** in solution if -52.1 ppm.

TABLE VI

Selected Parameters for Pentaoxyphosphoranes with Eight-Membered Rings



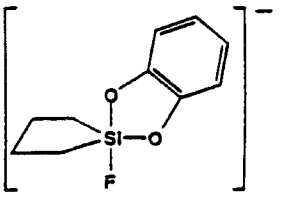
	X	Y	Z	R	% octa[a]	P–S, Å	δ(31P), ppm	ring conformn[b]	ring distortn, Å	ref[c]
K	Me	Me	S	Ph	44.1	2.880(1)	–81.16	twisted boat	1.20	10
L	*t*-Bu	Me	S	Ph	56.8	2.744(2)	–81.86	twisted boat	1.16	10
D	*t*-Bu	*t*-Bu	S	Ph	60.8	2.640(2)	–82.6	twisted boat	1.05	10
E	*t*-Bu	*t*-Bu	S	CH_2CF_3	64.5	2.504(3)	–82.44	sym boat		8
M	*t*-Bu	Me	S	CH_2CF_3	69.4	2.362(2)	–82.3	sym boat		12

	X	Y	Z	R	% SP[d]	P–S, Å	δ(31P), ppm	ring conformn	ref[c]
N	Me	Me	S	CH_2CF_3	11.0[e]	3.504(3)	–77.30	sym chair	8
O	*t*-Bu	Me	CH_2	CH_2CF_3	TBP[e]		–78.80	sym chair	8, 29
P	H	H	CH_2	CH_2CF_3	13.5[e]		–78.3	twisted boat	8

	% SP	P–S, Å	δ(31P), ppm	ring conformn	ring distortn, Å	ref[c]
U[f]	29	3.652(3)	–76.48	twisted boat	1.62	1b
		3.485(4)		twisted boat	1.55	

	% TBP[g]	Si–S, Å	δ(29Si), ppm	ring conformn		ref[c]
1	53	3.04(1)	–107.84	sym boat		this work
	43	3.11(1)	–99.35	twisted boat	1.39	

[a] Percent displacement from an ideal square pyramid to an octahedron. [b] Symmetric is abbreviated "sym". [c] See also ref 30 and 31 for a correlation of 31P shifts for cyclic oxyphosphoranes. [d] The numerical entries in this column represent percent displacements from a trigonal bipyramid (TBP) toward a square pyramid (SP).[32] [e] N and O have the rings placed diequatorially (e–e) in a TBP with a nonbonding P–S distance for N, whereas the ring in P is oriented in axial–equatorial sites. [f] Even though U has rings in twisted-boat conformations, there are no P–S interactions. [g] The disiloxane 1 has silicon atoms distorted from a tetrahedral geometry toward a TBP.



T

Ring Conformations

The eight-membered rings of the disiloxane **1** do not have the same conformation (Figure 2). The ring containing Si1 and S1, which has the shortest of the two Si–S distances, is in a symmetrical *syn* conformation; i.e., both the silicon atom and the sulfur atom are on the same side of the hypothetical plane defined by the remaining ring atoms. A pseudo mirror plane contains the silicon and sulfur atoms. The ring containing Si2 and S2 is in a twist *syn* conformation. This ring geometry may also be referred to that of a twisted tub. Atoms O7, C71, C51, and C52, which form the base of the tub, are coplanar to within ±0.044(30) Å. The remaining ring atoms (Si2, O5, S2, and C72) are displaced from this plane in the same direction by distances of 1.076(10), 0.874(22), 1.208(10), and 0.512(32) Å, respectively.

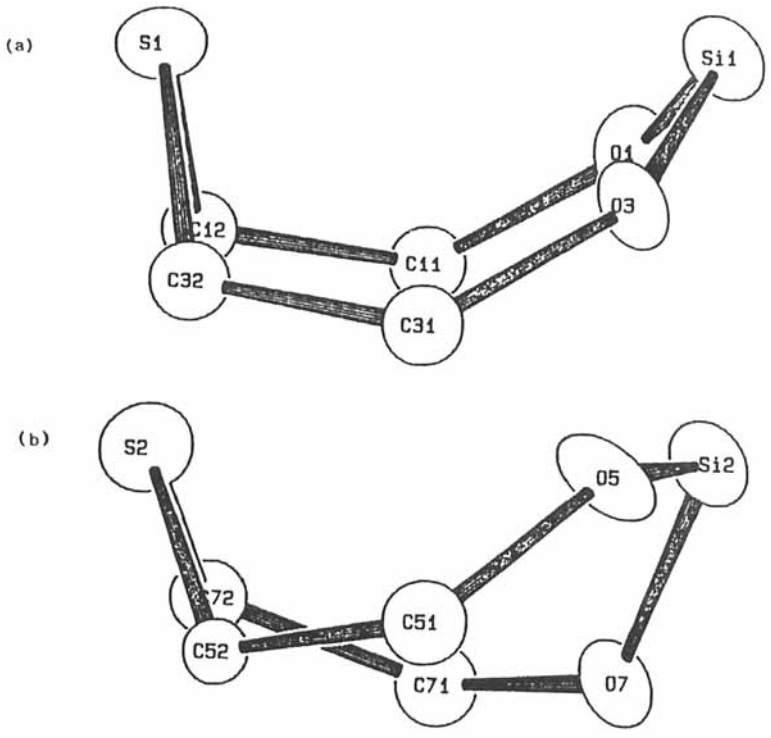


FIGURE 2 ORTEP plots showing the conformations of the eight-membered rings in **1**: (a) ring containing Si1; (b) ring containing Si2.

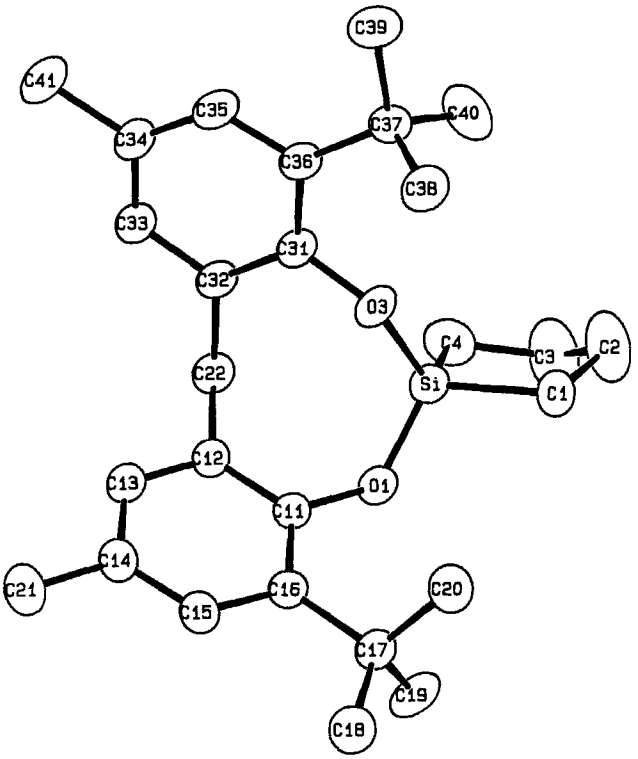


FIGURE 3 ORTEP plot of $CH_2[(t\text{-Bu})MeC_6H_2O]_2Si(CH_2)_4$ (**3**) with thermal ellipsoids at the 30% probability level. H atoms are omitted for clarity.

The eight-membered ring of the silane **3**, like that of Si2 in **1**, is in a twisted *syn* conformation (Figure 4), and the ring has no pseudo-C_s symmetry. Alternatively, the ring may be described as a twisted boat or tub. The atoms forming the base of the tub (C31, O3, C11, and C12) are coplanar to within ±0.053(3) Å. The remaining ring atoms (Si, O1, C22, and C32) are displaced from this plane in the same direction by distances of 1.076(1), 0.750(2), 1.020(4), and 0.368(4) Å, respectively.

The five-membered ring of **3** is in a twisted conformation (pseudo-C_2 symmetry) rather than an envelope conformation (pseudo-C_s symmetry). Specifically, atoms C2 and C3 are displaced in opposite directions by distances of 0.243(6) and 0.278(7) Å, respectively, from the plane defined by the remaining ring atoms (Si, C1, and C4).

In comparison with oxyphosphoranes having sulfur-containing eight-membered rings (Table VI), we note that all members showing P–S interactions and hexacoordination have either symmetrical or twisted-tub (boatlike) ring conformations,[8,10,12] while observance of a symmetrical chair in an *anti* conformation for the ring in **N** accompanies diequatorial ring placement in a trigonal-bipyramidal geometry.[8] In the recently reported bicyclic oxyphosphorane **U**, having no P–S interaction, the X-ray structure[1b] (shown here in schematic fashion) has the rings in axial–equatorial sites of TBP, similar to the phosphorane **P**[8] having a methylene

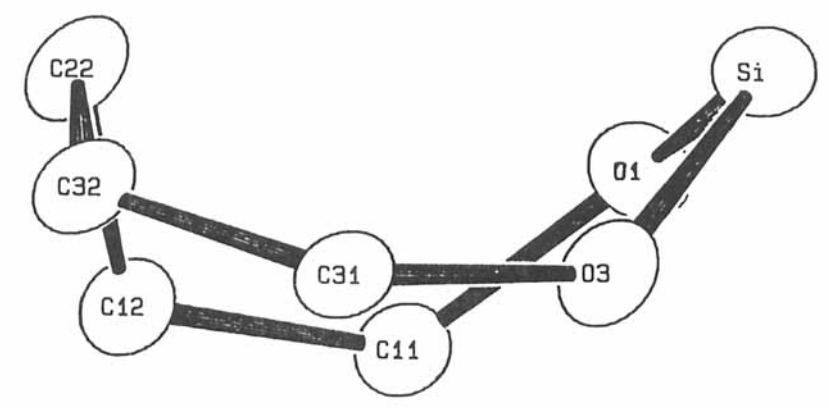
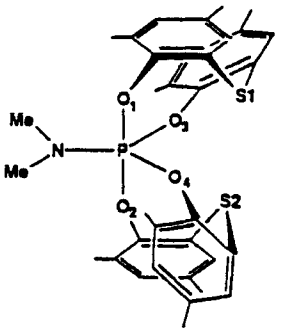


FIGURE 4 ORTEP plot showing the conformation of the eight-membered ring in **3**.



U [1b]

bridge in place of sulfur (Table VI). Both of these compounds have the eight-membered rings in very twisted boatlike conformations. The variety of ring conformations found is illustrated in Figure 5 for the phosphoranes **N**, **U**, and **E**, having rings in the symmetrical (*anti*), twisted-boat (*syn*), and symmetrical-boat (*syn*) conformations, respectively.

It is possible to obtain an approximate relation between the extent of either the P–S or Si–S interaction and ring distortion, by making use of the atom displacements from mean planes of the eight-membered rings. With reference to this calculation for the disiloxane **1** above and Figure 2b, the sum of the displacements of O5 and C72 from the mean plane found for O7, C71, C51, and C52 for the distorted ring containing atoms Si2 and S2 is 1.39 Å. The accompanying Si2–S2 distance is 3.11(1) Å. This same type of calculation for the oxyphosphoranes **K**, **L**, and **D** (Table VI) showing twisted-boat rings in *syn* conformations[10] gives 1.20, 1.16, and 1.05 Å, respectively, while the values for the rings of the bicyclic phosphorane **U**[1b] having a–e ring orientations in a TBP are 1.62 Å for the ring containing S1 (Figure 5b) and 1.55 Å for the ring containing S2 (Figure 5c). Although small differences are not significant, it is seen that the lowest values centered between 1.05 and 1.20 Å for **D**, **L**, and **K** have the shortest P–S distances (2.64–2.89 Å, Table VI), while the largest sums (1.55 and 1.62 Å) are present for the rings in

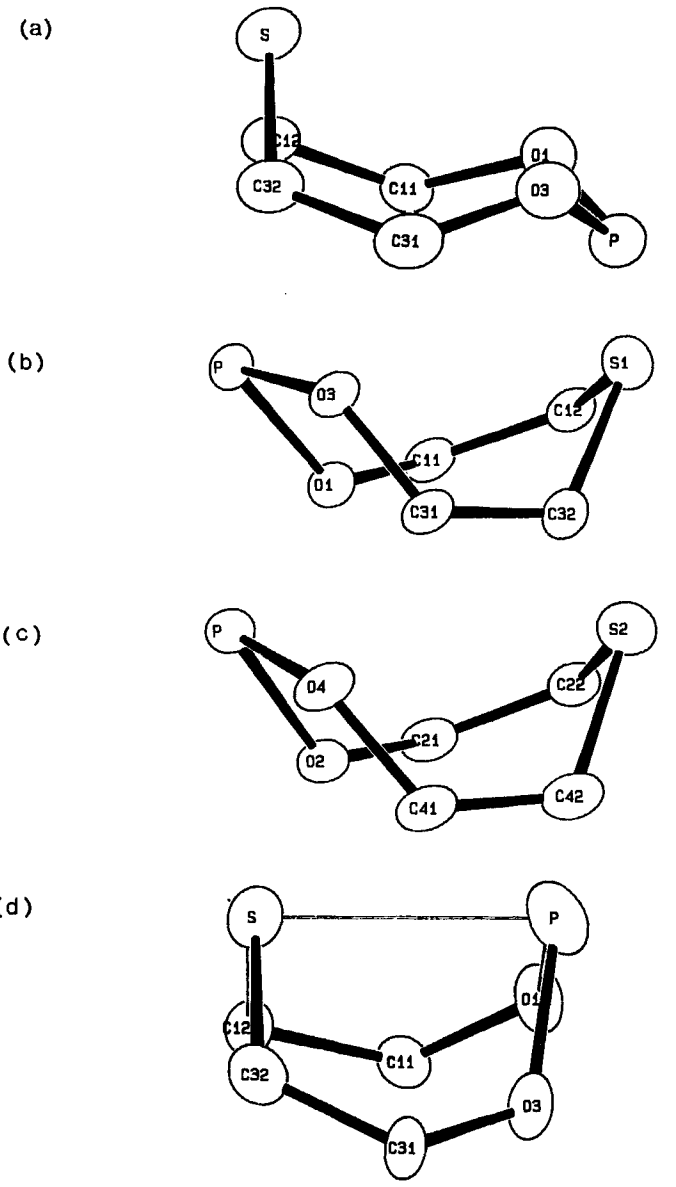


FIGURE 5 ORTEP plot showing the conformation of the eight-membered ring for (a) $S(Me_2C_6H_2O)_2P(OCH_2CF_3)_3(N)$, (b) $[S(Me_2C_6H_2O)_2]_2PNMe_2(U)$, for the ring containing S1, (c) U, for the ring containing S2, and (d) $S[(t\text{-}Bu)_2C_6H_2O]_2P(OCH_2CF_3)_3$ (E).

phosphorane U, which has the longest P–S distance of these derivatives (3.485(4) and 3.652(3) Å, respectively).

The latter trend of increasing ring distortion with increasing central atom–sulfur distance is consonant with the trend $T_d \rightarrow$ TBP calculated earlier, showing that, in the disiloxane **1**, the displacement for the very symmetrical ring arrangement at the Si1 atom was 53% toward pentacoordination while that for the more distorted

ring geometry at Si2 resulted in a lower Si–S interaction, giving a 43% displacement toward pentacoordination.

CONCLUSION

The use of both bond parameters at silicon and ring distortions as well as ^{29}Si chemical shift data support appreciable Si–S interaction in the disiloxane **1**. The geometry is intermediate between tetrahedral and trigonal bipyramidal and represents the first example of a sulfur interaction promoting pentacoordination for a tetraoxysilane. This conclusion receives support from structural comparisons with and ring distortions of oxyphosphoranes having the same type of eight-membered ring containing a sulfur atom, capable of P–S interaction. A series of these derivatives shows increased coordination from a square pyramid toward an octahedron.

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Supplementary Material Available: Atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen atom parameters for **1** (Tables S1–S4) and **3** (Tables S5–S8) (21 pages). Ordering information is given on any current masthead page.

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