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Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01003

Acyclic Substituent Effects on the Molecular Structure of Cyclic-Containing Five-Coordinated Anionic Silicates.[1,2] A Model for Nucleophilic Substitution at Silicon

ROBERT R. HOLMES,* ROBERTA O. DAY, V. CHANDRASEKHAR, JOHN J. HARLAND,[3]
and JOAN M. HOLMES

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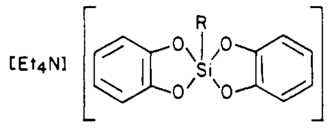
The new five-coordinated cyclic anionic silicates $[(C_6H_4O_2)_2Si\text{-}1\text{-}Np][Et_4N]$ (**1**), $[(C_6H_4O_2)_2Si\text{-}n\text{-}Bu][Et_4N]$ (**2**), and $[(C_6H_4O_2)_2Si\text{-}t\text{-}Bu][Et_4N]$ (**3**) were synthesized and their X-ray molecular structures determined. The structures show increasing displacement from the trigonal bipyramid toward the rectangular pyramid in the order **1** (30.8%) < **2** (63.8%) < **3** (91.4%), on the basis of unit vectors. The order parallels the increase in electron donor ability of the acylic ligand, 1-Np < *n*-Bu < *t*-Bu, and is aided in the case of **3** by the steric effect associated with the *tert*-butyl group. The role of five-coordinated anionic silicates as models for nucleophilic substitution at silicon is stressed, and support is given for a retention mechanism proceeding by way of a low-energy trigonal bipyramid–square pyramid interchange, similar to that documented for phosphorus compounds. ^1H and ^{13}C NMR spectra are tentatively assigned. **1** crystallizes in the orthorhombic space group $Pna2_1$ with $a = 22.367$ (7) Å, $b = 11.193$ (3) Å, $c = 10.793$ (2) Å, and $Z = 4$. **2** crystallizes in the trigonal space group $R\bar{3}c$, hexagonal setting, with $a = b = 20.594$ (8) Å, $c = 30.735$ (7) Å, and $Z = 18$. **3** crystallizes in the monoclinic space group $P2_1$ with $a = 9.598$ (4) Å, $b = 13.063$ (4) Å, $c = 10.632$ (4) Å, $\beta = 113.04$ (3)°, and $Z = 2$. The final conventional unweighted residuals are 0.078 (**1**), 0.094 (**2**), and 0.064 (**3**).

Introduction

In understanding the factors that control site occupancies and geometrical distortions of the ligands attached to the silicon center of five-coordinated anionic compounds, previous studies have centered on the role of ring unsaturation,[4,5] ring substitution,[4-6] relative ligand electronegativity,[7-9] and lattice effects including hydrogen bonding.[4,5,10] The conclusions for silicon regarding factors favoring the formation of the square or rectangular pyramid (RP) compared to the formation of the inherently more stable trigonal bipyramid (TBP) parallel those obtained for phosphoranes. In general, the electronegativity rule governing the ligand positions in these two geometrical forms is followed, i.e., that the most electronegative groups occupy axial sites in the TBP[11] and basal sites in the RP,[11,12] as is the requirement that to achieve a RP structure two unsaturated five-membered rings with like atoms in any one ring directly attached to the central atom must be present.[13,14] It also was found, as with phosphoranes,[15,16] that the presence of electron-withdrawing ring substituents on the spirocyclic framework favored formation of the rectangular pyramid for five-coordinated silicon.[4,5]

A "rule" that has been subject to some exceptions for phosphoranes[17] concerns the role of the acyclic ligand. Usually, the occupancy of the fifth position by large groups of low electronegativity promotes the formation of the rectangular pyramid. This is in keeping with the VSEPR model,[18] which suggests that the lower the electronegativity of the acylic ligand, the greater will be the electron pair repulsion between the resulting ligand bond with those of the neighboring ring atom bonds.

To test this criteria for formulation of a RP structure, a series of five-coordinated anionic silicates containing the same cyclic component and cation portion was synthesized and their molecular structures were determined. The acyclic ligand was varied from α-naphthyl, to *n*-butyl, to *tert*-butyl, in the cyclic derivatives, **1-3**, respectively.

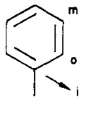


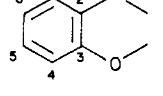
1, R=α-Np
2, R=*n*-Bu
3, R=*t*-Bu

The results of this study are compared with similar studies on pentacoordinated derivatives of other main-group elements.

Experimental Section

Proton NMR spectra were recorded with a Varian Model XL-300 NMR spectrometer operating at 300 MHz using pulse FT methods. The samples were dissolved in CD_3CN. ^{29}Si NMR spectra were obtained on the XL-300 spectrometer at 59.6 MHz operating in the Fourier transform mode. Samples were prepared in acetonitrile (0.5-1.0 M) containing $Cr(acac)_3$ (0.04 M) to reduce relaxation times. ^{13}C NMR were recorded on a Varian Model XL-200 NMR spectrometer operating in the FT mode at 50.31 MHz. The samples were dissolved in acetonitrile. Deuterio-chloroform was used for locking, with Me_4Si as the internal standard. The chemical shifts are reported in ppm; shifts downfield to Me_4Si are positive. The ^{13}C assignments are tentative. They are based on reported trends and general additivity rules for organosilicon compounds.[19,20] The numbering system for the aromatic substituents used for the ^{13}C assignments is shown:





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(1) Pentacoordinated Molecules. 62. Part 61: Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.*, preceding paper in this issue.
(2) Presented at the Seventh International Symposium on Organosilicon Chemistry, Kyoto, Japan, Sept 1984; Chemical Society of Japan, Abstr. 2C1110.
(3) This work represents in part a portion of: Harland, J. J. Ph.D. Thesis, University of Massachusetts, Amherst, MA.
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Materials. Catechol (Aldrich) was used as received. Tetraethylammonium halides (Eastman Kodak) were dried over P_2O_5 under vacuum before use. Solvents were purified by conventional methods. *tert*-Butyltrichlorosilane and *n*-butyltrimethoxysilane (Petrarch) were used as received.

Preparations. (a) Triethylammonium Bis(*o*-phenylenedioxy)-1-naphthylsilicate(IV), [($C_6H_4O_2$)$_2$SiC$_{10}$H$_7$][Et$_3$NH] (4). 1-Naphthyltriethoxysilane (prepared from the reaction of lithiated naphthalene with ethylorthosilicate[21]) (3.0 g, 10 mmol) was added to a methanol solution (10 mL) of catechol (2.2 g, 20 mmol) and triethylamine (2.0 g, 20 mmol). After standing 2 h at room temperature, the reaction mixture was refrigerated overnight (yield 3.8 g, 81%).

(b) Tetraethylammonium Bis(*o*-phenylenedioxy)-1-naphthylsilicate(IV), [($C_6H_4O_2$)$_2$SiC$_{10}$H$_7$][Et$_4$N] (1). To a solution of **4** (2.0 g, 4.2 mmol) in acetonitrile (20 mL) was added tetraethylammonium bromide (0.87 g, 4.2 mmol). The solution was stirred to dissolve the solids and then evaporated to obtain the cation-exchanged product, **1**. After treatment with water (50 mL), the undissolved solid was collected and dried under vacuum. The latter solid was recrystallized from acetonitrile and ether (1:2): yield 1.8 g (87%); mp 177.5–179 °C. ^{1}H NMR (δ): 0.85 (t, NCCH$_3$, 12 H), 2.68 (q, NCH_2CH$_3$, 8 H), 6.60 (m, 8 H), 7.55 (m, 5 H), 8.65 (m, 2 H). ^{29}Si NMR(δ): −84.9. ^{13}C NMR for the anion (δ): C$_i$, 140.81; C$_1$/C$_4$, 109.90; C$_2$/C$_3$, 149.62; C$_5$/C$_6$, 116.33. ^{13}C NMR for the cation (δ): NC*C*, 6.10; N*C*C, 51.20. The chemical shifts for the naphthyl group appear at δ 135.50, 132.18, 131.39, 129.58, 127.07, 126.68, 124.18, and 123.71. Anal. Calcd for $C_{30}H_{35}O_4NSi$: C, 71.82; H, 7.03; N. 2.79. Found: C, 71.2; H, 6.95; N, 2.90.

(c) Tetraethylammonium Bis(*o*-phenylenedioxy)-*n*-butylsilicate(IV), [($C_6H_4O_2$)$_2$Si-*n*-Bu][Et$_4$N] (2). *n*-Butyltrimethoxysilane (2.79 g, 15.7 mmol) was dissolved in acetonitrile (75 mL) and methanol (75 mL). Catechol (3.45 g, 31.3 mmol) and triethylamine (1.59 g, 15.7 mmol) were added to the above solution, and the reaction mixture was heated for 16 h. Removal of solvent yielded a solid. It was reacted with tetraethylammonium chloride (2.59 g, 15.7 mmol) in acetonitrile (50 mL) for 2 h at room temperature. Solvent was removed from the above reaction mixture, yielding a solid. It was washed quickly with water (2 × 20 mL) to remove triethylamine hydrochloride. (Water seems to cause hydrolysis of the organosilicon compound.) The remaining solid was redissolved in acetonitrile and dried (Na_2SO_4). After filtration and removal of solvent, compound **2** was obtained: yield 1.35 g (20%); mp 175–185 °C dec. It was recrystallized from a mixture of acetonitrile and ether (1:1) at room temperature. ^{1}H NMR (δ): 0.54 (m, 2 H), 0.75 (m, 2 H), 1.2 (m, 17 H), 3.10 (q, NCH_2CH$_3$, 8 H), 6.53 (*m*, 8 H). ^{13}C NMR for the anion (δ): Si*C*H$_2$*C*H$_2$*C*H$_2$*C*H$_3$, 6.71, 13.87, 17.19, 26.52; C$_1$/C$_4$, 110.44; C$_2$/C$_3$, 150.65; C$_5$/C$_6$, 117.73. ^{13}C NMR for the cation (δ): NC*C*, 7.007; N*C*C, 51.90. Anal. Calcd for $C_{24}H_{37}O_4NSi$: C, 66.78; H, 8.64; N, 3.25. Found: C, 66.71; H, 8.77; N, 3.16.

(d) Tetraethylammonium Bis(*o*-phenylenedioxy)-*tert*-butylsilicate(IV), [($C_6H_4O_2$)$_2$Si-*t*-Bu][Et$_4$N] (3). *tert*-Butyltrichlorosilane (3.46 g, 18.1 mmol) was reacted with catechol (3.98 g, 36.2 mmol) and triethylamine (7.33 g, 72.4 mmol) in dry benzene (200 mL) at the reflux temperature for 12 h. It was filtered and the solvent removed to yield a solid that was treated with tetraethylammonium chloride (3.0 g, 18.1 mmol) in acetonitrile (50 mL) and stirred at room temperature for 30 min. Removal of acetonitrile in vacuo yielded a solid that was washed with water (3 × 50 mL) to remove metathetically exchanged Et$_3$NH$^+$Cl$^-$. The remaining solid was redissolved in acetonitrile, dried over anhydrous magnesium sulfate, and filtered, and the solvent was removed to yield a solid that was recrystallized from acetonitrile and ether (1:1) at room temperature: yield 6.60 g (84.6%); mp 225 °C dec. ^{1}H NMR (δ): 0.76 (s, 9 H, CCH$_3$), 1.16 (t, NCCH$_3$, 12 H), 3.11 (q, NCH_2CH$_3$, 8 H), 6.50 (m, 8 H). ^{29}Si NMR (δ): −75.8. ^{13}C NMR for the anion (δ): *C*CH$_3$, 22.85 C*C*H$_3$, 28.36; C$_1$/C$_4$, 109.54; C$_2$/C$_3$, 150.88; C$_5$/C$_6$, 116.21. ^{13}C NMR for the cation (δ): NC*C*, 6.53; N*C*C, 51.53. Anal. Calcd for $C_{24}H_{37}O_4NSi$: C, 66.78; H, 8.64; N, 3.25. Found: C, 66.75; H, 8.70; N, 3.20.

X-ray Studies. All X-ray crystallographic studies were done on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$ = 0.709 30 Å, $\lambda(K\alpha_2)$ = 0.713 59 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[22]

Crystals were mounted in sealed thin-walled glass capillaries as a precaution against moisture sensitivity. Diffraction data were collected in the θ–2θ scan mode for $2° \leq 2\theta_{\text{Mo K}\bar{\alpha}} \leq 50°$ for **1** and **3** and for $2° \leq 2\theta_{\text{Mo K}\bar{\alpha}} \leq 43°$ for **2**. No corrections were made for absorption. The structures were solved by using a combination of direct methods (MULTAN) and standard difference Fourier techniques and were refined by using full-matrix least squares.[23]

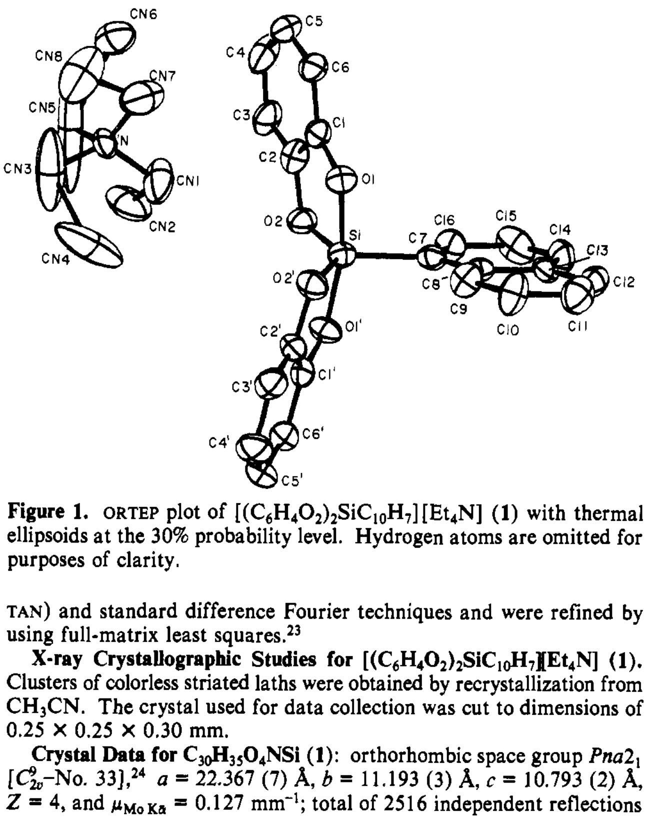

Figure 1. ORTEP plot of [($C_6H_4O_2$)$_2$SiC$_{10}$H$_7$][Et$_4$N] (**1**) with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for purposes of clarity.

X-ray Crystallographic Studies for [($C_6H_4O_2$)$_2$SiC$_{10}$H$_7$][Et$_4$N] (1). Clusters of colorless striated laths were obtained by recrystallization from CH$_3$CN. The crystal used for data collection was cut to dimensions of 0.25 × 0.25 × 0.30 mm.

Crystal Data for $C_{30}H_{35}O_4NSi$ (1): orthorhombic space group $Pna2_1$ [C_{2v}^9–No. 33],[24] a = 22.367 (7) Å, b = 11.193 (3) Å, c = 10.793 (2) Å, Z = 4, and $\mu_{\text{Mo K}\bar{\alpha}}$ = 0.127 mm^{-1}; total of 2516 independent reflections (+h, +k, +l) measured.

The 36 independent non-hydrogen atoms were refined anisotropically. The 15 independent aromatic hydrogen atoms were included in the refinement as fixed isotropic scatterers with calculated coordinates that were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. Hydrogen atoms of the cation, which suffer from either high thermal motion or unresolvable static disorder,[25] were omitted from the refinement. The final agreement factors[26] were R = 0.078 and R_w = 0.095 for the 1588 reflections having $I \geq 2\sigma_I$. A final difference Fourier showed a maximum density of 0.56 e/Å^3.

X-ray Crystallographic Studies for [($C_6H_4O_2$)$_2$Si-*n*-Bu][Et$_4$N] (2). Large colorless hexagonal prismatic needles obtained by recrystallization from CH$_3$CN/Et$_2$O (1:1) diffract very poorly. The crystal used for data collection was cut normal to the needle axis and had a maximum distance across the base of 0.38 mm and a height of 0.40 mm.

Crystal Data for $C_{24}H_{37}O_4NSi$ (2): trigonal space group $R\bar{3}c$ [D_{3d}^6–No. 167][27] hexagonal setting, $a = b$ = 20.594 (8) Å, c = 30.735 (7) Å, Z = 18, $\mu_{\text{Mo K}\bar{\alpha}}$ = 0.125 mm^{-1}; total of 1543 independent reflections (+h, +k, +l) measured. The *n*-butyl group is disordered about a 2-fold axis, and the four independent atoms comprising this group were refined isotropically in half-occupancy. The 14 remaining independent non-hydrogen atoms were refined anisotropically. Hydrogen atoms were omitted from the refinement. The final agreement factors[26] were R = 0.094 and R_w = 0.084 for the 679 reflections having $I \geq 2\sigma_I$. A final difference Fourier synthesis showed a maximum density of 0.273 e/Å^3.

X-ray Crystallographic Studies for [($C_6H_4O_2$)$_2$Si-*t*-Bu][Et$_4$N] (3). Large colorless irregular laths were obtained by recrystallization from CH$_3$CN/Et$_2$O (1:1). The crystal used for data collection was cut to the dimensions of 0.33 × 0.33 × 0.40 mm.

Crystal Data for $C_{24}H_{37}O_4NSi$ (3): monoclinic space group $P2_1$ [C_2^2–No. 4],[28] a = 9.598 (4) Å, b = 13.063 (4) Å, c = 10.632 (4) Å, β

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(23) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from ref 24 (1974, Vol. IV, pp 72–98). Real and imaginary dispersion corrections for Si and O were taken from the same source (pp 149–150).

(24) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 119.

(25) Since the carbon atoms of the cation were poorly defined and anisotropic refinement led to poor thermal ellipsoids and poor geometry for these atoms, the final refinement was repeated treating these atoms as isotropic scatterers. There was no significant change observed in the geometry of the anion, which is of interest, and we chose to report the results of the anisotropic refinement.

(26) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2 \sum w|F_o|^2\}^{1/2}$. For **1** and **3**, these values are for the configuration having the lowest R_w.

(27) Reference 24, p 275.

Table I. Atomic Coordinates in Crystalline $[(C_6H_4O_2)_2SiC_{10}H_7][Et_4N]$ (**1**)[a]

atom type[b]	10^4x	10^4y	10^4z
Si	1217 (1)	7889 (2)	3889[c]
O1	1813 (2)	8920 (5)	3940 (7)
O2	813 (2)	8906 (5)	3073 (7)
O1′	538 (2)	7059 (5)	4037 (7)
O2′	1314 (3)	7774 (6)	5454 (7)
N	945 (3)	12316 (7)	6464 (9)
C1	1702 (4)	9893 (8)	3236 (10)
C2	1128 (5)	9899 (9)	2745 (10)
C3	913 (5)	10813 (8)	2034 (11)
C4	1291 (6)	11729 (10)	1808 (16)
C5	1856 (5)	11764 (9)	2267 (12)
C6	2072 (4)	10855 (8)	2983 (10)
C1′	440 (4)	6715 (8)	5204 (11)
C2′	871 (4)	7136 (8)	6037 (11)
C3′	870 (5)	6862 (9)	7304 (11)
C4′	380 (6)	6172 (10)	7730 (12)
C5′	−61 (5)	5778 (10)	6916 (12)
C6′	−38 (4)	6063 (9)	5666 (12)
C7	1594 (4)	6754 (8)	2825 (9)
C8	2066 (4)	5961 (8)	3184 (10)
C9	2308 (5)	5938 (9)	4352 (10)
C10	2745 (5)	5128 (9)	4680 (12)
C11	2967 (4)	4335 (10)	3772 (15)
C12	2759 (4)	4371 (9)	2587 (13)
C13	2307 (4)	5160 (8)	2275 (10)
C14	2085 (5)	5204 (10)	1050 (10)
C15	1645 (5)	5960 (13)	732 (10)
C16	1396 (5)	6748 (9)	1621 (10)
CN1	947 (7)	11131 (14)	6001 (29)
CN2	175 (6)	11253 (15)	5127 (15)
CN3	673 (11)	12593 (21)	7598 (16)
CN4	688 (7)	11040 (24)	8265 (20)
CN5	535 (18)	13014 (38)	5845 (21)
CN6	1132 (6)	13700 (10)	4584 (15)
CN7	1569 (12)	12466 (16)	6310 (51)
CN8	1742 (7)	13475 (14)	7727 (22)

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

Table II. Selected Bond Lengths (Å) and Angles (deg) in $[(C_6H_4O_2)_2SiC_{10}H_7][Et_4N]$ (**1**)[a,b]

	Lengths		
Si–O1	1.763 (6)	O1–C1	1.351 (11)
Si–O2	1.700 (6)	O2–C2	1.364 (11)
Si–O1′	1.789 (5)	O1′–C1′	1.335 (11)
Si–O2′	1.708 (7)	O2′–C2′	1.374 (11)
Si–C7	1.909 (10)		
	Angles		
O1–Si–O2	88.9 (3)	Si–O1′–C1′	111.9 (6)
O1–Si–O1′	168.3 (3)	Si–O2′–C2′	113.6 (6)
O1–Si–O2′	85.6 (3)	Si–C7–C8	125.1 (7)
O1–Si–C7	96.9 (3)	Si–C7–C16	115.6 (7)
O2–Si–O1′	86.7 (3)	O1–C1–C2	112.8 (8)
O2–Si–O2′	129.1 (3)	O1–C1–C6	128.9 (9)
O2–Si–C7	111.6 (4)	O2–C2–C1	112.0 (8)
O1′–Si–O2′	88.9 (3)	O2–C2–C3	125 (1)
O1′–Si–C7	94.7 (3)	O1′–C1′–C2′	113.4 (9)
O2′–Si–C7	119.3 (4)	O1′–C1′–C6′	128 (1)
Si–O1–C1	111.8 (5)	O2′–C2′–C1′	112.2 (9)
Si–O2–C2	113.9 (6)	O2′–C2′–C3′	124 (1)

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

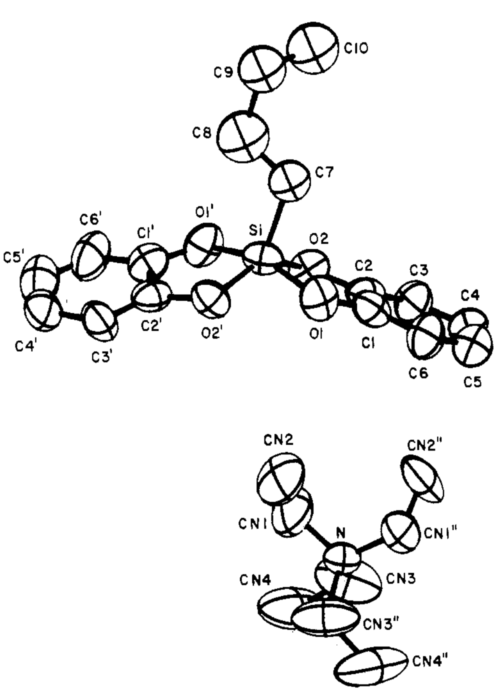

Figure 2. ORTEP plot of $[(C_6H_4O_2)_2Si\text{-}n\text{-}Bu][Et_4N]$ (**2**) with thermal ellipsoids at the 30% probability level. Only one of the two 2-fold related half *n*-butyl groups is shown. For the anion, primed atoms are related to unprimed ones by $-x, y - x, 1.5 - z$. For the cation, primed atoms are related to unprimed ones by $-x, y - x, 0.5 - z$.

Table III. Atomic Coordinates in Crystalline $[(C_6H_4O_2)_2Si\text{-}n\text{-}Bu][Et_4N]$ (**2**)[a]

atom type[b]	10^4x	10^4y	10^4z
Si	0[c]	6573 (3)	7500[c]
O1	−626 (7)	6106 (7)	7062 (3)
O2	−680 (6)	5939 (5)	7850 (3)
N	0[c]	6186 (8)	2500[c]
C1	−1325 (11)	5595 (11)	7197 (6)
C2	−1360 (11)	5481 (10)	7657 (6)
C3	−2027 (12)	4955 (11)	7879 (6)
C4	−2663 (13)	4562 (11)	7606 (9)
C5	−2616 (15)	4638 (15)	7143 (9)
C6	−1964 (14)	5160 (14)	6936 (7)
C7[d]	−180 (27)	7432 (22)	7396 (15)
C8[d]	398 (29)	8063 (29)	7608 (18)
C9[d]	298 (30)	8864 (27)	7490 (24)
C10[d]	−369 (35)	8655 (35)	7742 (17)
CN1	648 (13)	6925 (12)	2624 (11)
CN2	896 (12)	7535 (11)	2413 (11)
CN3	−220 (16)	5619 (13)	2880 (6)
CN4	379 (18)	5478 (14)	3009 (8)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2. [c] Fixed. [d] Half-occupancy.

= 113.04 (3)°, $Z = 2$, $\mu_{\text{Mo K}\bar{\alpha}} = 0.128$ mm^{-1}; total of 2258 independent reflections ($+h,+k,\pm l$) measured.

The methyl groups of the *tert*-butyl group are rotationally disordered, with each of the three independent carbon atoms having two possible positions. These atoms were refined isotropically as six independent atoms having half-occupancy. The 27 remaining independent non-hydrogen atoms were refined anisotropically. The 16 independent aromatic and methylene hydrogen atoms were treated in the same manner as described for **1**. Methyl hydrogen atoms were omitted from the refinement. The final agreement factors[26] were $R = 0.064$ and $R_w = 0.083$ for the 1823 reflections having $I \geq 2\sigma_I$. A final difference Fourier synthesis showed a maximum density of 0.42 e/Å^3.

Results

The atom-labeling scheme for **1** is shown in the ORTEP plot of Figure 1. Atomic coordinates are given in Table I, and selected bond lengths and angles are given in Table II. The corresponding material for **2** is given in Figure 2 and in Tables III and IV. The corresponding material for **3** is given in Figure 3 and in Tables V and VI. Hydrogen atom parameters, thermal parameters, additional bond lengths and angles, and deviations from selected least-squares mean planes are provided as supplementary material.

Discussion

Synthesis. The anionic bis(*o*-phenylenedioxy)-substituted silicates, **1**–**3**, represent new compounds. They were all synthesized

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(28) Reference 24, p 79.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) in Crystalline [($C_6H_4O_2$)$_2$Si-*n*-Bu][Et_4N] (**2**)[a,b]

	Lengths		
Si–O1	1.78 (1)	O1–C1	1.35 (2)
Si–O2	1.729 (9)	O2–C2	1.37 (2)
Si–C7	2.01 (3)		
	Angles		
O1–Si–O2	88.1 (5)	O2′–Si–C7	111 (2)
O1–Si–O1′	159.4 (8)	Si–O1–C1	113 (1)
O1–Si–C7	87 (1)	Si–O2–C2	114 (1)
O2–Si–O1′	84.7 (5)	O1–C1–C2	112 (2)
O2–Si–O2′	139.0 (8)	O1–C1–C6	127 (2)
O2–Si–C7	109 (2)	O2–C2–C1	111 (2)
O1′–Si–C7	113 (1)	O2–C2–C3	125 (2)

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

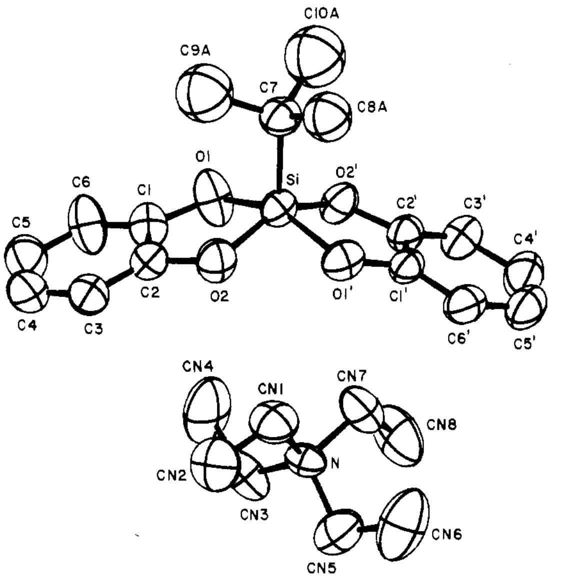

Figure 3. ORTEP plot of [($C_6H_4O_2$)$_2$Si-*t*-Bu][Et_4N] (**3**) with thermal ellipsoids at the 50% probability level. Only one set of positions (C8A, C9A, C10A) for the rotationally disordered methyl groups is shown. Hydrogen atoms have been omitted for purposes of clarity.

by the reaction of catechol with either RSi(OR′)$_3$ or RSiCl$_3$ in the presence of Et$_3$N in a suitable solvent (eq 1).

$$\begin{array}{l}2C_6H_4(OH)_2 + RSiR'_3 + xEt_3N \longrightarrow [(C_6H_4O_2)_2SiR][Et_3NH] + 3R'H\cdot yEt_3N \\ \qquad\qquad\qquad\qquad\qquad \Big\downarrow {\scriptstyle Et_4N^+Cl^-} \\ \qquad\qquad\qquad [(C_6H_4O_2)_2SiR][Et_4N] + Et_3NH^+Cl^- \qquad (1)\end{array}$$

	R	R′	*x*	*y*
1	1-Np	OEt	1	0
2	*n*-Bu	OMe	1	0
3	*t*-Bu	Cl	4	1

Carbon-13 NMR. The chemical shifts of the carbons attached to the oxygen atoms of aromatic dioxy substituents are the most downfield. In all of the compounds, **1**–**3**, they appear as a single absorption within a very narrow range (149.62–150.88 ppm). These values are very close to the values observed for the related anionic silicates described in the preceding paper,[1] underscoring the fact that the carbon chemical shifts in pentacoordinated anionic organosilicates are probably dependent on the electronegativity of the substituents attached and to the general arrangement of atoms around silicon.

Basic Structures. The catechol ligands of **1** and **3** are related by a pseudo-2-fold axis coincident with the Si–C7 bond. To facilitate examination of this pseudosymmetry, atoms have been labeled so that the primed ones are pseudo-2-fold related to the unprimed ones having the same label. In the case of **2**, the Si and N atoms lie on crystallographic 2-fold axes and primed atoms are actually 2-fold related to unprimed ones. The *n*-butyl group is disordered about the 2-fold axis upon which the Si atom lies.

Table V. Atomic Coordinates in Crystalline [($C_6H_4O_2$)$_2$Si-*t*-Bu][Et_4N] (**3**)[a]

atom type[b]	10^4x	10^4y	10^4z
Si	7053 (2)	8425[c]	2184 (1)
O1	8898 (4)	8738 (4)	2304 (5)
O2	7426 (5)	7166 (4)	1896 (5)
O1′	5826 (4)	7881 (4)	2869 (4)
O2′	7387 (5)	9415 (3)	3378 (4)
N	9375 (5)	6673 (4)	6564 (4)
C1	9602 (7)	7940 (6)	1974 (6)
C2	8773 (7)	7047 (6)	1727 (7)
C3	9306 (9)	6147 (6)	1409 (8)
C4	10720 (10)	6188 (7)	1363 (8)
C5	11553 (8)	7048 (7)	1618 (8)
C6	10993 (8)	7946 (7)	1931 (9)
C1′	5621 (5)	8475 (6)	3831 (5)
C2′	6512 (6)	9363 (5)	4138 (6)
C3′	6544 (8)	10023 (6)	5134 (7)
C4′	5614 (9)	9799 (7)	5852 (7)
C5′	4733 (7)	8936 (7)	5572 (7)
C6′	4740 (7)	8228 (6)	4539 (6)
C7	5765 (7)	8965 (6)	476 (6)
C8A[d]	4098 (18)	8655 (13)	91 (17)
C9A[d]	5701 (29)	10155 (21)	479 (27)
C10A[d]	6172 (24)	8554 (20)	−701 (23)
C8B[d]	4843 (25)	8089 (17)	−482 (22)
C9B[d]	4538 (27)	9631 (21)	725 (24)
C10B[d]	6648 (22)	9588 (17)	−244 (19)
CN1	8504 (8)	6321 (7)	5082 (7)
CN2	8880 (10)	5243 (6)	4759 (8)
CN3	11079 (8)	6631 (6)	6897 (9)
CN4	11582 (12)	7277 (8)	6016 (13)
CN5	9100 (10)	5987 (6)	7570 (8)
CN6	7385 (12)	5966 (10)	7367 (12)
CN7	8875 (9)	7757 (6)	6676 (9)
CN8	9660 (10)	8272 (7)	8070 (9)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3. [c] Fixed. [d] Half-occupancy.

The geometry about the Si atom for all three structures lies on the coordinate connecting a trigonal bipyramid (TBP) having O1 and O1′ in axial positions and a rectangular pyramid (RP) having four basal oxygen atoms and an apical carbon atom, where the carbon atom is pivotal in the Berry pseudorotation process.[29] With use of the dihedral angle method to assess displacement,[30] **1** is displaced 27.8% (30.8% using unit vectors) from the TBP to the RP. For **2** and **3**, these values are 59.3% (63.8% using unit vectors) and 88.6% (91.4% using unit vectors), respectively.

That **3** is quite close to being rectangular pyramidal is seen in the near coplanarity of the oxygen atoms; O1, O1′, O2, and O2′ are coplanar to within ±0.03 Å, while the Si atom is displaced 0.471 Å out of this plane in the direction of C7 (plane 3, Table K; supplementary material).

For **1** and **2**, residual trigonal-bipyramidal character is seen in the Si–O bond lengths. For **1**, the Si–O$_{ax}$ bond lengths have an average value of 1.776 (8) Å while the Si–O$_{eq}$ bond lengths have an average value of 1.704 (9) Å. For **2**, Si–O$_{ax}$ is 1.78 (1) Å while Si–O$_{eq}$ is 1.729 (9) Å. The difference between these values for the two structures follows the degree of displacement toward the RP: 0.08 Å for **1** and 0.05 Å for **2**.

Structural Comparisons. The five-coordinated anionic silicate salts, **1**–**3**, differ in composition only in the kind of acyclic ligand present. The order of structural displacement in this series, from the TBP toward the RP, **3** > **2** > **1**, parallels the order of electron-donating ability of the fifth ligand, *t*-Bu > *n*-Bu > 1-Np.

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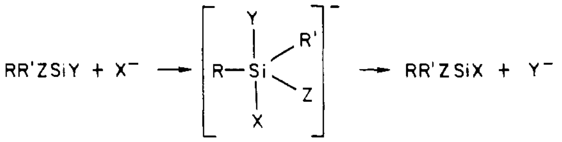
(29) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(30) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

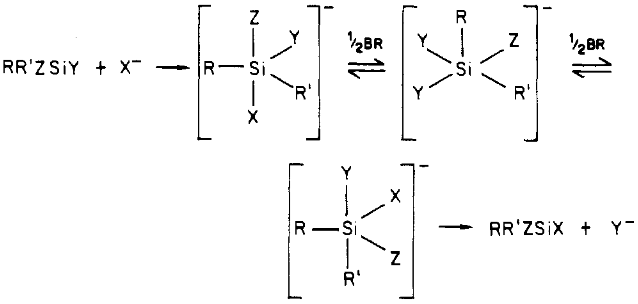
This order of structural displacement is consistent with earlier results on phosphoranes[13,31,32] where it was found that the presence of an acyclic ligand of low electronegativity and large size favors the formation of a rectangular pyramid. In the case of **3**, the large steric size of the *tert*-butyl group may aid the attainment of the RP form. This composition for the phosphorane, $(C_6H_4O_2)_2P$-*t*-Bu, has a structure[33] displaced 86% toward the RP[34] along the Berry pseudorotational coordinate, nearly the same as that for **3**, 91.4%, on the basis of unit vectors.

Model for Nucleophilic Substitution. Five-coordinated anionic silicates are isoelectronic with phosphoranes, and in the same sense that the structures of phosphoranes serve as models for nucleophilic substitution of phosphorus compounds,[35] anionic silicate compositions should prove useful as models of nucleophilic displacement for reactions of silicon compounds.[36]

By analogy with the mechanisms postulated for phosphorus compounds,[35,37] one factor that will influence the importance of an inversion



or retention mechanism



will be the ease of the trigonal-bipyramid–square-pyramid interchange embodied in the retention mechanism (i.e., a Berry pseudorotation process). We have demonstrated by our present and related work[1,4,5] that the structures of pentacoordinated anionic silicates readily traverse the trigonal-bipyramidal–square-pyramidal coordinate, comparably to that of phosphoranes,[14,30,32] indicating this is a low energy pathway.

The attractiveness of the above retention mechanism for silicon compounds is that the entering and departing groups do so from the axial positions of a trigonal bipyramid, which are the positions having the longer presumably weaker bonds. As shown in the accompanying paper,[1] the axial–equatorial bond length difference for trigonal bipyramids is about 0.1 Å for $RSiO_4^-$ derivatives.

Table VI. Selected Bond Lengths (Å) and Angles (deg) in $[(C_6H_4O_2)_2Si$-*t*-$Bu][Et_4N]$ (**3**)[a,b]

	Lengths		
Si–O1	1.772 (4)	O1–C1	1.361 (7)
Si–O2	1.736 (5)	O2–C2	1.383 (7)
Si–O1′	1.759 (4)	O1′–C1′	1.357 (7)
Si–O2′	1.752 (4)	O2′–C2′	1.376 (6)
Si–C7	1.888 (6)		
	Angles		
O1–Si–O1′	151.0 (2)	Si–O2–C2	113.4 (4)
O1–Si–O2	87.8 (2)	Si–O1′–C1′	113.5 (4)
O1–Si–O2′	83.3 (2)	Si–O2′–C2′	114.1 (4)
O1–Si–C7	104.1 (3)	O1–C1–C2	113.0 (5)
O1′–Si–O2	84.7 (2)	O1–C1–C6	126.9 (6)
O1′–Si–O2′	87.7 (2)	O2–C2–C1	112.3 (6)
O1′–Si–C7	104.9 (2)	O2–C2–C3	125.8 (6)
O2–Si–O2′	146.7 (2)	O1′–C1′–C2′	113.2 (4)
O2–Si–C7	106.7 (3)	O1′–C1′–C6′	125.5 (6)
O2′–Si–C7	106.7 (3)	O2′–C2′–C1′	111.2 (5)
Si–O1–C1	112.8 (4)	O2′–C2′–C3′	126.4 (6)

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

An alternative retention mechanism leading to a five-coordinated activated state in which a nucleophilic attack occurs adjacent to a departing group involves at least one equatorial bond. If the nucleophile approaches along an equatorial direction, considerable bond rearrangement energy is required. If the nucleophile approaches more conventionally along the axial direction, an equatorial bond involving the departing group must stretch and eventually rupture. At present, experimental evidence for either of these types of structural distortions is lacking, and a theoretical treatment indicates that these are relatively higher energy processes.[38]

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Registry No. **1**, 96346-89-3; **2**, 96293-12-8; **3**, 96293-14-0; **4**, 96346-90-6; 1-naphthyltriethoxysilane, 17938-06-6; catechol, 120-80-9; tetraethylammonium bromide, 71-91-0; *n*-butyltrimethoxysilane, 1067-57-8; tetraethylammonium chloride, 56-34-8; *tert*-butyltrichlorosilane, 18171-74-9.

Supplementary Material Available: Table A, anisotropic thermal parameters for **1**; Table B, fixed hydrogen atom parameters for **1**; Table C, thermal parameters for **2**; Table D, thermal parameters for **3**; Table E, fixed hydrogen atom parameters for **3**; Table F, additional bond lengths and angles for **1**; Table G, additional bond lengths and angles for **2**; Table H, additional bond lengths and angles for **3**; Table I, deviations from selected least-squares mean planes for **1**; Table J, deviations from selected least-squares mean planes for **2**; Table K, deviations from selected least-squares mean planes for **3**; and a listing of observed and calculated structure factor amplitudes for **1**–**3** (27 pages). Ordering information is given on any current masthead page.

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