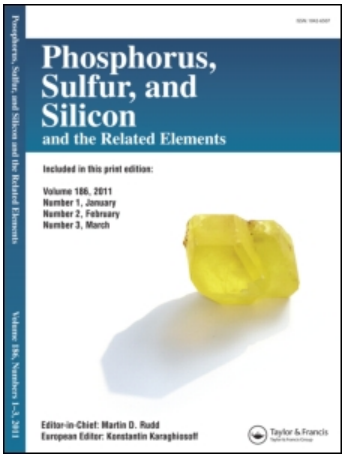

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SYNTHESIS AND MOLECULAR STRUCTURE OF HYDROGEN-BONDED CYCLIC ANIONIC SILICATES ISOELECTRONIC WITH PHOSPHORANES. STRUCTURAL PRINCIPLES OF FIVE-COORDINATED SILICON

Robert R. Holmes[a]; Roberta O. Day[a]; John J. Harland[a]; Joan M. Holmes[a]
[a] Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

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SYNTHESIS AND MOLECULAR STRUCTURE OF HYDROGEN-BONDED CYCLIC ANIONIC SILICATES ISOELECTRONIC WITH PHOSPHORANES. STRUCTURAL PRINCIPLES OF FIVE-COORDINATED SILICON[1,2]

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

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

(Received September 9, 1983)

The new five-coordinated silicon compounds, pyridinium bis(2,3-naphthalenediolato)phenylsilicate(IV), $[(C_{10}H_6O_2)_2SiPh][C_5H_6N]$, **11**, pyridinium bis(1,2-benzenediolato)-1-naphthylsilicate(IV), $[(C_6H_4O_2)_2Si\text{-}C_{10}H_7][C_5H_6N]$, **12**, and pyridinium bis(1,2-benzenediolato)(2- and 4-chlorophenyl)silicate(IV) (2-Cl, 0.85; 5-Cl, 0.15), $[(C_6H_4O_2)_2SiC_6H_4Cl][C_5H_6N]$, **13**, were synthesized and their X-ray structures determined. The structure of **11** is nearly an ideal rectangular pyramid (RP) and **12** is displaced about halfway between the RP and trigonal bipyramid (TBP), while **13** is closer to a TBP. A quantitative assessment of these and related pentacoordinated cyclic anionic silicate structures reveals a continuous change in ring Si—O bond lengths that vary from 1.78 (axial) and 1.68 Å (equatorial) for the idealized TBP to 1.73 Å (basal) for the RP. The results for these compounds, all of which follow the Berry pseudorotational coordinate, suggest a structural nonrigidity at least as great as found for phosphoranes. The structures attained for **11–13**, which exhibit different degrees of hydrogen bonding with the pyridinium cation, are discussed in terms of electron delocalization of the ring system in **11** and the implication of steric effects of the unique ligand in **12** and **13**. Both **11** and **13** crystallize in the monoclinic space group $P2_1/n$ with a = 10.959 (4) Å, b = 20.332 (7) Å, c = 11.448 (3) Å, β = 99.07 (2)°, and Z = 4 for **11** and a = 9.397 (3) Å, b = 20.335 (8) Å, c = 11.067 (5) Å, β = 102.82 (3)°, and Z = 4 for **13**. **12** crystallizes in the monoclinic space group Cc with a = 16.529 (3) Å, (b) = 17.603 (5) Å, c = 8.293 (3) Å, β = 111.63 (3)°, and Z = 4.

INTRODUCTION

As evident in the preceding article,[5] pentacoordinated bicyclic silicates isoelectronic with phosphoranes form a range of solid-state structures extending from the trigonal bipyramid (TBP) to the square or rectangular pyramid (RP) along the Berry pseudorotational coordinate.[5] In establishing this coordinate, structural principles[6–9] learned from studies on phosphoranes[10] were utilized as a guide in synthesizing five-coordinated anionic silicates whose structures would exist between the two principal geometries, particularly those toward the square pyramid. The latter geometry is one which we characterized for silicon only recently.[11] Schomburg[12–14] has concentrated attention on five-coordinated anionic silicates having structures nearer the TBP. Considering the meagerness of the structures elucidated thus far, it is somewhat surprising to see[4] a rather uniform distribution of structural distortions between the two representative pentacoordinated geometries.

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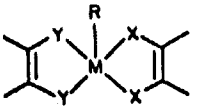
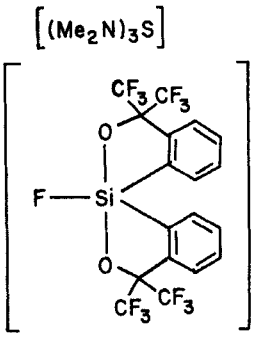
The most important principle[6,15,16] in forming the square pyramid for phosphoranes concerns the presence of two unsaturated five-membered rings containing like atoms in any one ring directly bonded to the central atom. This is illustrated in **1** where X and Y may be the same or different.



1

We have found this same principle applicable to silicon.[4] In fact, present data indicate that it is a general principle applicable to most pentacoordinated main-group elements.[17]

Although it was shown[4] that the angles around silicon assumed changes across the series of five-coordinated derivatives which closely mimiced the Berry intramolecular ligand exchange coordinate, it is also necessary to establish in what way



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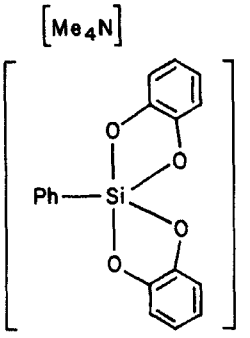

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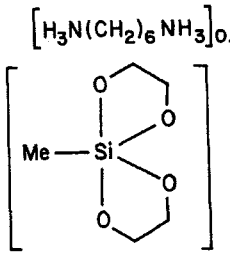

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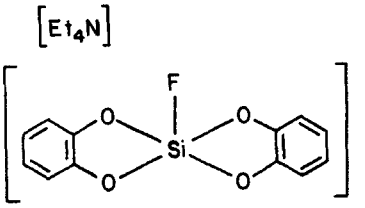

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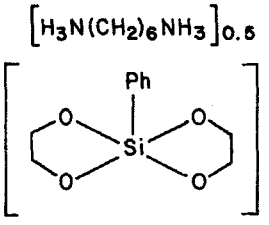

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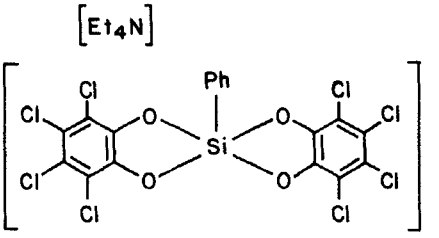

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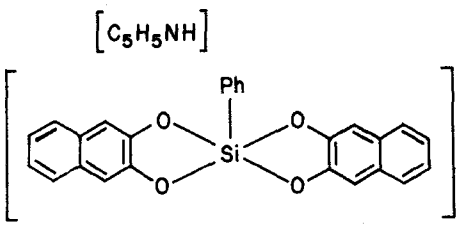

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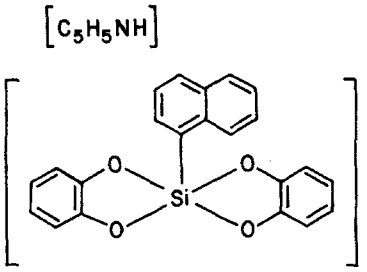

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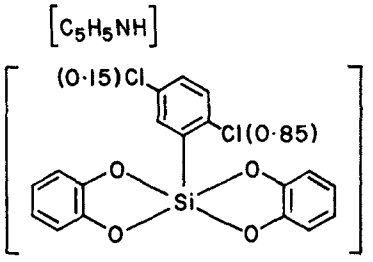


13

bond distance variations correspond to this coordinate. To accomplish the latter, it is necessary to study a series of derivatives containing the same kind of ligand directly attached to silicon. The acyclic derivatives $[PhCH_2NMe_3][SiF_5]$, **2**,[14] $[(n\text{-}Pr)_4N][PhSiF_4]$, **3**,[12] and $[Me_4N][Ph_2SiF_3]$, **4**,[14] all contain fluorine atoms but the cyclic derivatives **5–10**[4,11,13,18,19] all possess oxygen atoms.

To provide an adequate basis set, this paper reports the synthesis and X-ray structural characterization of the pentacoordinated cyclic anionic silicates **11–13.** The naphthalene phenylsilicate $[(C_{10}H_6O_2)_2SiPh][C_5H_6N]$, **11,** was prepared to examine the structural effect of the use of a bulkier ligand in forming the cyclic system. Since little knowledge exists concerning the influence of the acyclic ligand R in **1,** in forming either a trigonal bipyramid or square pyramid, the five-coordinated silicates $[(C_6H_4O_2)_2SiC_{10}H_7][C_5H_6N]$, **12,** and $[(C_6H_4O_2)_2SiC_6H_4Cl][C_5H_6N)$, **13** containing the α-naphthyl and chlorobenzene, respectively, were chosen for study. These derivatives contain the same ring system and cation construction.

In addition to isolating specific features in an attempt to uncover structural principles for five-coordinated silicon, it is of interest to ascertain the similarity

with principles established for phosphoranes[6-9,16] and to decide whether such principles are applicable in forming intermediates and transition states in silicon reaction mechanisms. Many reaction mechanisms of silicon compounds have been postulated to proceed by way of a pentacoordinated state, but the description of these activated complexes remains uncertain.[20] In the case of Phosphorus chemistry, a diversity of reaction mechanisms has been correlated with structural principles from phosphoranes.[7]

EXPERIMENTAL

Preparation of Pyridinium Bis(2,3-naphthalenediolato)phenylsilicate(IV), $[(C_{10}H_6O_2)_2SiPh][C_5H_6N]$, **11**. A solution of 1.6 g (10 mmol) of 2,3-dihydroxynaphthalene, Aldrich, in 3 mL of pyridine was placed in a 25-mL round-bottom flask fitted with a reflux condenser. The apparatus was flushed with dry nitrogen and heated in an oil bath, under a positive nitrogen pressure, to 90°C. To this was added 0.99 g (5 mmol) of phenyltrimethoxysilane. The mixture was heated at 90°C for 10 min and then allowed to slowly cool to room temperature. Crystallization occurred during this cooling. The melting range of the product **11** was 247–248°C (yield 1.95 g (78%)). Anal. Calcd for $C_{31}H_{23}NO_4Si$: C, 74.23; H, 4.62; N, 2.79. Found: C, 73.87; H, 4.61; N, 2.75.

Preparation of Pyridinium Bis(1,2-benzenediolato)-1-naphthylsilicate(IV), $[(C_6H_4O_2)_2SiC_{10}H_7][C_5H_6N]$, **12**. 1-Naphthyltriethoxysilane (prepared from the reaction of lithiated naphthalene with ethylorthosilicate[21]) (3.0 g, 10 mmol) was added to a solution of catechol (2.3 g, 20 mmol) in pyridine (0.82 g, 10 mmol) and the mixture heated for 10 min at 90°C under a dry nitrogen atmosphere. The precipitate **12** that formed upon cooling was filtered under suction and recrystallized from boiling acetonitrile: yield 3.65 g (78%); melting range, 187–189°C. Anal. Calcd for $C_{27}H_{21}NO_4Si$: C, 71.82; H, 4.69; N, 3.10. Found: C, 71.39; H, 4.52; N, 3.03.

Preparation of Pyridinium Bis(1,2-benzenediolato)(2- and 5-chlorophenyl)silicate(IV) (2-Cl, 0.85; 5-Cl, 0.15), $[(C_6H_4O_2)_2SiC_6H_4Cl][C_5H_6N]$, **13**. (Chlorophenyl)triethoxysilane, Petrarch, (2.5 g, 9 mmol), was added to a solution of catechol (2.0 g, 18 mmol) in pyridine (3.5 mL) and the mixture heated for 10 min at 90°C under a dry nitrogen atmosphere. Evaporation of the solvent from the reaction mixture gave a yellow solid, **13**, which was recrystallized from a 1:2:4 pyridine/acetonitrile/ether solution: melting range, 202.5–204°C. Anal. Calcd for $C_{23}H_{18}ClNO_4Si$:C, 63.37; H, 4.16; N, 3.21. Found: C, 63.12; H, 4.21; N, 3.01.

Crystallography. All X-ray crystallographic studies were done by using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1)$ = 0.709 30 Å, $\lambda(K\alpha_2)$ = 0.71359 Å) at an ambient temperature of 23± 2°C. Details of the experimental and computational procedures have been described previously.[22]

X-ray Crystallographic Studies for **11**. The crystal used for the X-ray studies was a colorless triangular plate (edge lengths 0.35 × 0.40 × 0.40 mm, thickness 0.20 mm) which was cut from a polycrystalline mass and mounted inside of a sealed, thin-walled glass capillary as a precaution against moisture sensitivity.

Crystal data: $[(C_{10}H_6O_2)_2SiPh][C_5H_6N]$, uniquely determined space group $P2_1/n$ (alternate setting of $P2_1/c$, $[C_{2h}^5$—No. 14][23]), a = 10.959 (4) Å, b = 20.332 (7) Å, c = 11.448 (3) Å, β = 99.07 (2)°, Z = 4, $\mu_{MoK\bar{\alpha}}$ = 0.137 mm^{-1}. A total of 4066 independent reflections ($+h$, $+k$, $\pm l$) were measured by using the θ–2θ scan mode for $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 48.5°$. No corrections were made for absorption.

The structure was solved by using a combination of direct methods (MULTAN) and differences Fourier techniques and was refined by using full-matrix least squares.[24] The placement of the pyridinium N atom was deduced from the relative magnitudes of the thermal parameters, treating all six of the pyridinium non-hydrogen atoms as carbon. The 37 independent non-hydrogen atoms were refined anisotropically, while the 23 hydrogen atoms were included in the refinement as fixed isotropic scatterers, with calculated coordinates which were updated as refinement converged so that the final C—H bond lengths were 0.98 Å, and the N—H bond length was 0.90 Å. The final agreement factors[25] were R = 0.044 and R_w = 0.056 for the 2695 reflections having $I \geq 2\sigma_I$. A final difference Fourier synthesis showed a maximum density of 0.191 e/Å.

X-ray Crystallographic Studies for **12**. Crystals of 12 are colorless, unstable large rods which degrade when exposed to air or exposed to X-rays. By starting with a fresh crystal mounted inside of a sealed, thin-walled glass capillary, it was possible to take a data set before the onset of degradation. The crystal used for data collection was a fragment having dimensions of 0.23 × 0.35 × 0.38 mm, which was cut from a larger crystal.

Crystal data: $[(C_6H_4O_2)_2SiC_{10}H_7][C_5H_6N]$, monoclinic space group *Cc*, [C_s^4—No. 9],[26] from 2/m diffraction symmetry, extinctions, and successful solution and refinement, a = 16.529 (3) Å, b = 17.603 (5) Å, c = 8.293 (3) Å, β = 111.63 (3)°, Z = 4, $\mu_{MoK\bar{\alpha}}$ = 0.197 mm^{-1}. A total of 1287 independent reflections ($+h$, $+k$, $\pm l$) were measured by using the θ–2θ scan mode for 2° ≤ $2\theta_{MoK\bar{\alpha}}$ ≤ 43°. No corrections were made for absorption.

The structure was solved and refined as described for **11**, but with 23 independent anisotropic non-hydrogen atoms and 21 independent, fixed hydrogen atoms. The final agreement factors[27] were R = 0.036 and R_w = 0.045 for the 1129 reflections having $I \geq 2\sigma_I$. A final difference Fourier synthesis showed a maximum density of 0.128 e/Å^3.

X-ray Crystallographic Studies for **13**. Crystals of **13** are colorless needles which diffract poorly. The crystal used for the X-ray studies, cut from a larger crystal, had dimensions of 0.13 × 0.23 × 0.38 mm and was mounted inside of a sealed, thin-walled glass capillary as a precaution against moisture sensitivity.

Crystal data: $[(C_6H_4O_2)_2SiC_6H_4Cl][C_5H_6N]$, uniquely determined space group $P2_1/n$ (alternate setting of $P2_1/c$, [C_{2h}^5—No. 14][22]) a = 9.397 (3) Å, b = 20.335 (8) Å, c = 11.067 (5) Å, β = 102.82 (3)°, Z = 4, $\mu_{MoK\bar{\alpha}}$ = 0.286 mm^{-1}. A total of 2357 independent reflections ($+h$, $+k$, $\pm l$) were measured for 2° ≤ $2\theta_{MoK\bar{\alpha}}$ ≤ 43°. No corrections were made for absorption.

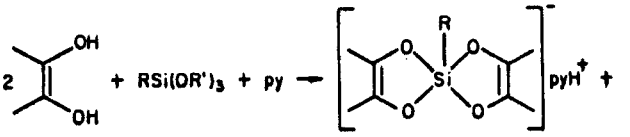
The structure was solved and refined as described for **11**. During this process it became evident that the crystal consisted of a disordered mixture of molecules containing either an ortho- or a meta-substituted chlorophenyl group. The occupancy of the predominant chlorine atom Cl1 was refined, while the occupancy of the other chlorine atom Cl2 was reset between cycles so that the total combined occupancy was 1. The final refinement was therefore based on 30 anisotropic non-hydrogen atoms in full occupancy, two partial anisotropic Cl atoms having occupancies of 0.848 (5) and 0.152 (5), and 17 fixed isotropic hydrogen atoms. The final agreement factors were R = 0.058 and R_w = 0.063 for the 1313 reflections having $I \geq 2\sigma_I$. A final difference Fourier synthesis showed a maximum density of 0.336 e/Å^3.

RESULTS AND DISCUSSION

Syntheses

The spirocyclic five-coordinated anionic silicates **11**–**13** represent newly synthesized substances. Their preparation follows the general scheme illustrated in eq 1 which consisted of a condensation reaction of an *o*-dihydroxyaryl moiety with a trialkoxyarylsilane in pyridine solution. This reaction is similar to those used in the preparation of the related anionic silicates **9**[4] and **10**[4] but contrasts with the preparation of **8**.[11] The latter was synthesized[11] by the reaction of bis(*o*-phenylenedioxy)silane with $Et_4N^+F^-\cdot 2H_2O$ in acetonitrile (eq 2).

Recently, we discovered that discrete pentacoordinated anionic complexes of germanium (IV)[28] and tin(IV)[29] are formed by the reaction of the spirocyclic derivatives with halide ions, similar to the reaction in eq 2. In the case of the ger-



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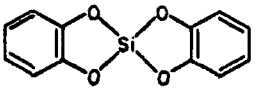


(2)

manium derivatives,[28] they were formed based on use of bis(*o*-phenylenedioxy)germanium (IV) dihydrate, $Ge(C_6H_4O_2)_2\cdot 2H_2O$, and bis(toluene-3,4-dithiolato)germanium(IV), $Ge(C_7H_6S_2)_2$. For the tin derivatives,[29] reaction of halide ions with bis(toluene-3,4-dithiolato)tin(IV), $Sn(C_7H_6S_2)_2$, led to the pentacoordinated salts. The germanium and tin species are isoelectronic with five-coordinated arsenic(V) and antimony(V) derivatives, respectively.

The use of alkyl or aryl substituted Ge(IV)[30,31] and Sn(IV)[32] halides in a reaction analogous to eq 1 gives cyclic pentacoordinated species retaining the alkyl or aryl groups.

Attempts to prepare additional anionic five-coordinated silicon species by way of eq 2 using other halide salts proved unsatisfactory. Reaction of the salts $Et_4N^+Cl^-$, n-$Bu_4N^+Cl^-$, and $Ph_4P^+Cl^-$ appeared to proceed in acetonitrile since solution of bis(*o*-phenylenedioxy)silane occurred in each case upon addition of the respective salt. However, only the starting materials were isolated upon concentrating the solution, which suggests a reversible dissociation.

Basic Structures

The atom labeling scheme and the molecular geometry for **11** are shown in Figure 1, while atomic coordinates for nonhydrogen atoms are given in Table I. The

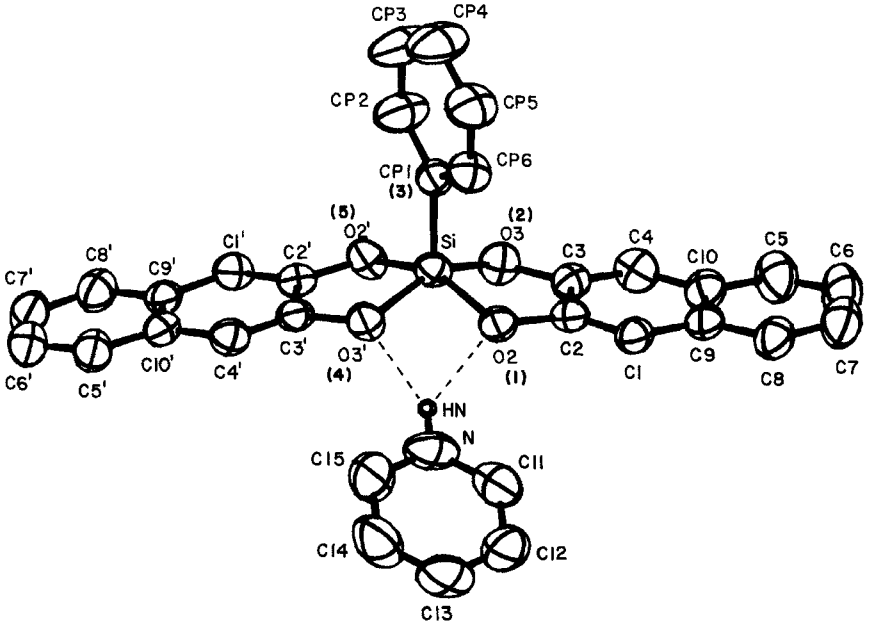


FIGURE 1 ORTEP plot of $[(C_{10}H_6O_2)_2SiPh][C_5H_6N]$, **11**, with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms, except HN which is shown as a sphere of arbitrary radius, are omitted for purposes of clarity.

TABLE I

Atomic Coordinates in Crystalline $[(C_{10}H_6O_2)_2SiPh][C_5H_6N]$, 11[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Si	2258.6 (8)	3563.4 (4)	3343.4 (8)
O2	2938 (2)	2786 (1)	3579 (2)
O3	3700 (2)	3870 (1)	3183 (2)
O2'	1672 (2)	4208 (1)	2434 (2)
O3'	920 (2)	3112 (1)	2803 (2)
C1	4964 (3)	2338 (2)	4341 (3)
C2	4198 (3)	2824 (2)	3853 (3)
C3	4640 (3)	3449 (2)	3604 (3)
C4	5867 (3)	3589 (2)	3797 (3)
C5	7996 (3)	3214 (2)	4571 (4)
C6	8780 (4)	2746 (3)	5118 (4)
C7	8335 (4)	2137 (2)	5413 (3)
C8	7101 (3)	1996 (2)	5148 (3)
C9	6256 (3)	2469 (2)	4591 (3)
C10	6700 (3)	3094 (2)	4304 (3)
C1'	−269 (3)	4573 (2)	1305 (3)
C2'	467 (3)	4123 (1)	1959 (3)
C3'	12 (3)	3494 (2)	2191 (3)
C4'	−1185 (3)	3325 (2)	1827 (3)
C5'	−3238 (3)	3639 (2)	737 (3)
C6'	−3991 (3)	4080 (2)	64 (4)
C7'	−3525 (3)	4688 (2)	−216 (3)
C8'	−2316 (3)	4851 (2)	169 (3)
C9'	−1516 (3)	4409 (2)	864 (3)
C10'	−1982 (3)	3787 (2)	1150 (3)
CP1	1996 (3)	3797 (2)	4865 (3)
CP2	1660 (4)	4421 (2)	5166 (3)
CP3	1451 (5)	4567 (2)	6302 (4)
CP4	1572 (5)	4084 (2)	7160 (4)
CP5	1911 (4)	3463 (2)	6888 (3)
CP6	2117 (3)	3324 (2)	5757 (3)
C11	2453 (4)	1382 (2)	2392 (4)
C12	2318 (4)	742 (2)	2082 (4)
C13	1172 (5)	497 (2)	1725 (4)
C14	178 (5)	896 (2)	1672 (4)
C15	343 (4)	1536 (2)	2001 (4)
N	1465 (4)	1756 (2)	2351 (3)

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

corresponding information for **12** and **13** is given in Figure 2 and Table II, and Figure 3 and Table III, respectively. Anisotropic thermal parameters, hydrogen atom parameters, additional bond lengths and angles, and deviations from some least-squares mean planes for **11**, **12**, and **13** are provided as supplementary material.

There is considerable variation in the structures of the spirocyclic anionic silicates **11–13**. While **11** is a rectangular pyramid (RP), the α-naphthyl derivative **12** is approximately halfway between the two limiting geometries and the (chlorophenyl)silicate **13** is nearer the trigonal bipyramid (TBP). Relative to the TBP, both **12** and **13** have two ring oxygen atoms (O1 and O1′) that may be considered axial and two ring oxygen atoms (O2 and O2′) and a carbon atom that occupy

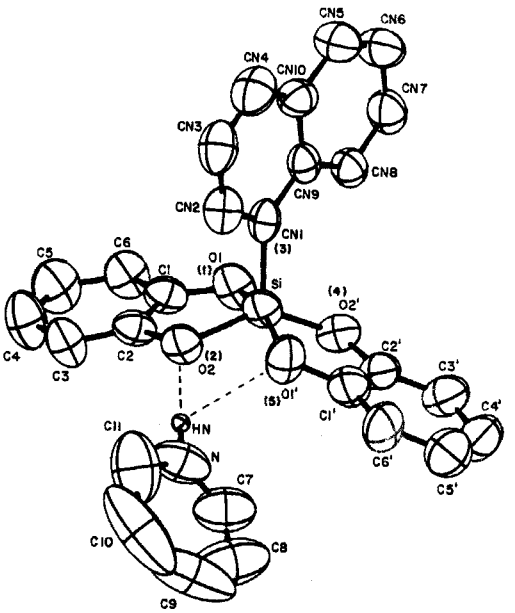


FIGURE 2 ORTEP plot of $[(C_6H_4O_2)_2SiC_{10}H_7)][C_5H_6N]$, **12**, with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms, except HN which is shown as a sphere of arbitrary radius, have been omitted for purposes of clarity.

TABLE II

Atomic Coordinates in Crystalline $[(C_6H_4O_2)_2SiC_{10}H_7][C_5H_6N]$, 12[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Si	2410[c]	7947 (1)	6220[c]
O1	2502 (3)	8058 (2)	4193 (5)
O2	1383 (3)	8361 (2)	5328 (5)
O1'	2022 (3)	7634 (2)	7833 (6)
O2'	2869 (3)	7064 (2)	6287 (5)
CN1	3201 (4)	8688 (3)	7502 (7)
CN2	2875 (4)	9267 (3)	8218 (8)
CN3	3378 (5)	9861 (4)	9156 (9)
CN4	4236 (6)	9914 (4)	9386 (9)
CN5	5518 (5)	9360 (4)	8970 (10)
CN6	5892 (5)	8807 (4)	8324 (10)
CN7	5391 (4)	8198 (4)	7402 (9)
CN8	4525 (4)	8161 (3)	7123 (8)
CN9	4106 (4)	8724 (3)	7779 (7)
CN10	4621 (4)	9342 (3)	8696 (8)
C1	1865 (4)	8499 (3)	3089 (8)
C2	1218 (4)	8679 (3)	3730 (7)
C3	522 (4)	9101 (4)	2804 (8)
C4	482 (5)	9385 (4)	1206 (9)
C5	1123 (5)	9233 (5)	591 (9)
C6	1816 (4)	8764 (4)	1513 (8)
C1'	2303 (4)	6928 (4)	8403 (8)
C2'	2790 (4)	6604 (3)	7547 (8)
C3'	3124 (5)	5870 (4)	7919 (10)
C4'	2933 (6)	5465 (4)	9182 (11)

TABLE II (*Continued*)

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
C5'	2449 (6)	5792 (5)	10024 (11)
C6'	2128 (5)	6530 (4)	9684 (9)
N	136 (4)	7792 (5)	6599 (8)
C7	71 (6)	7063 (6)	6622 (12)
C8	-447 (11)	6755 (7)	7210 (14)
C9	-945 (9)	7134 (13)	7727 (13)
C10	-977 (9)	7911 (14)	7754 (17)
C11	-365 (8)	8255 (6)	7075 (14)

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

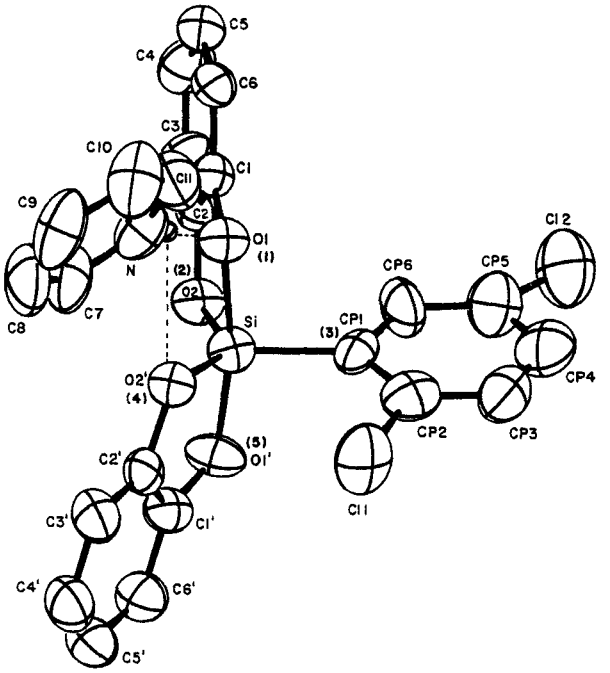


FIGURE 3 ORTEP plot of $[(C_6H_4O_2)_2SiC_6H_4Cl][C_5H_6N]$, **13**, with thermal ellipsoids shown at the 50% probability level. Both of the partial chlorine atoms are shown. Hydrogen atoms, except HN which is shown as a sphere of arbitrary radius, have been omitted for purposes of clarity.

TABLE III

Atomic Coordinates in Crystalline $[(C_6H_4O_2)_2SiC_6H_4Cl][C_5H_6N]$, 13[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
Cl2[c]	547 (20)	7579 (9)	3951 (18)
Cl1[d]	-3422 (3)	6590 (1)	6635 (3)
Si	3 (2)	6065 (1)	7847 (2)
O1	124 (4)	5338 (2)	6918 (4)
O2	1869 (4)	6068 (2)	8236 (4)

TABLE III (*Continued*)

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
O1′	−16 (5)	6656 (2)	8994 (4)
O2′	−1220 (5)	5615 (2)	8419 (4)
C1	1497 (8)	5232 (4)	6786 (6)
C2	2499 (8)	5644 (4)	7548 (6)
C3	3975 (8)	5628 (4)	7580 (8)
C4	4428 (9)	5164 (5)	6822 (9)
C5	3463 (10)	4749 (4)	6064 (7)
C6	1963 (9)	4775 (4)	6051 (6)
C1′	−933 (8)	6485 (4)	9737 (6)
C2′	−1661 (8)	5899 (4)	9409 (6)
C3′	−2630 (9)	5644 (4)	10031 (7)
C4′	−2894 (9)	5998 (5)	11048 (8)
C5′	−2164 (10)	6572 (5)	11391 (7)
C6′	−1172 (8)	6833 (4)	10752 (7)
CP1	−590 (8)	6628 (3)	6470 (7)
CP2	−2054 (9)	6824 (4)	5953 (8)
CP3	−2444 (11)	7238 (4)	4914 (9)
CP4	−1330 (15)	7476 (4)	4386 (9)
CP5	107 (13)	7295 (5)	4865 (10)
CP6	457 (10)	6887 (4)	5890 (8)
N	−1689 (7)	4306 (3)	7144 (9)
C7	−1897 (11)	4159 (5)	8244 (9)
C8	−2798 (14)	3678 (6)	8416 (9)
C9	−3534 (10)	3332 (5)	7408 (14)
C10	−3313 (12)	3497 (5)	6273 (11)
C11	−2388 (12)	3987 (5)	6139 (8)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3. [c] Occupancy = 0.152 (5). [d] Occupancy = 0.848 (5).

TABLE IV

Bond Lengths (Å) and Bond Angles (deg) about Silicon for 11, 12, and 13

	11	12	13
Si-1	1.750 (2)	1.734 (4)	1.820 (5)
Si-5	1.733 (2)	1.772 (4)	1.751 (5)
Si-2	1.734 (2)	1.742 (4)	1.710 (5)
Si-4	1.759 (2)	1.722 (4)	1.698 (5)
Si-3	1.871 (3)	1.875 (6)	1.888 (8)
1-Si-5	152.1 (1)	160.4 (2)	168.4 (3)
2-Si-4	150.9 (1)	137.8 (2)	130.5 (3)
3-Si-1	106.5 (1)	100.2 (2)	94.6 (3)
3-Si-5	102.6 (1)	99.2 (2)	97.0 (3)
3-Si-2	102.1 (1)	108.4 (2)	107.7 (3)
3-Si-4	105.7 (1)	113.8 (2)	121.6 (3)
1-Si-2	88.2 (1)	87.8 (2)	87.5 (2)
4-Si-5	88.5 (1)	88.4 (2)	89.0 (3)
1-Si-4	83.9 (1)	86.5 (2)	84.5 (2)
2-Si-5	85.5 (1)	83.3 (2)	89.4 (3)
%TBP → RP[b]	95.5_{av} (97.6_{av})	56.2 (58.7)	30.4 (33.2)
δ_{14} (unit)	1.2	21.9	35.5

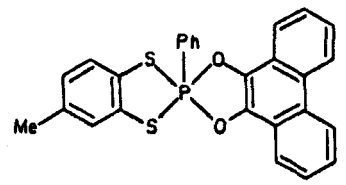
[a] The identities of the atoms 1 through 5 are given in the ORTEP plots of Figures 1, 2, and 3 for 11, 12, and 13, respectively. [b] The first entries are for calculations based on actual atomic coordinates. The entries in parentheses are derived by using unit vectors in place of actual bond lengths.

equatorial positions. Relative to the RP, the ring system in **12** and **13** shows distortions from the basal plane with the carbon atom situated apically. The four oxygen atoms comprising the basal plane for **11** are coplanar to within ±0.01 Å (Table J, plane 1), with the silicon atom displaced 0.429 Å out of the basal plane in the direction of the apical carbon atom.

With use of the method described in the preceding paper[4] to measure structural distortion, **11** shows an average displacement from the TBP toward the RP of 97.6% (based on unit bond distances), **12** is positioned 58.7% toward the RP, and **13** is displaced 33.2% (Table IV). All are located along the Berry intramolecular ligand exchange coordinate and follow local C_s^2 symmetry as determined from the positions of the five atoms attached to silicon.

Ligand Influences

The achievement of the rectangular-pyramidal geometry apparently is aided by the use of large unsaturated ring systems. The phosphorane **14**[33] and arsorane **15**[34]



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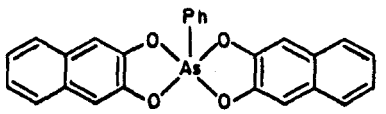

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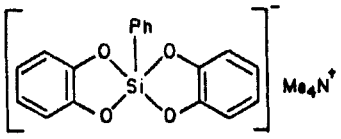
represent the least distorted rectangular pyramids for each of these elements. The same holds with five-coordinated silicon as seen from the nearly ideal RP character of **11.** Presumably, the greater electron delocalization offered by these ligands, which would reduce electron pair repulsions for the bonds attached to the central atom, may be a factor in stabilizing the RP structure. On the basis of VSEPR theory,[35] the reduced repulsions would decrease the energy of the less stable RP relative to the TBP.

The rationale for the specific structures of **12** and **13** is less clear. Both pentacoordinated anions for these substances show distances for nonbonded atoms, implicating steric terms. For **13,** the dihedral angle between the plane of the phenyl ring and the equatorial plane as defined by atoms Si, O2, O2′ and CP1 (coplanar to within ±0.03 Å) is 10.0° (planes 2 and 7, Table L). The near coplanarity of these two planes brings the ortho chloro atom Cl1 into close proximity with O2′. The effect of this crowding can be seen in the equatorial angles CP1—Si—02′ and CP1—Si—02 which have values of 121.6 (3)° and 107.7 (3)°, respectively. The distance between 02′ and Cl1 is 3.209 (6) Å, which is essentially equal to the van der Waals sum of 3.20 Å.[36]

For **12,** the dihedral angle between the plane of the naphthyl group and the

equatorial plane Si, 02, 02′ and CN1 (coplanar to within ±0.01 Å) is 29.9° (planes 2 and 9, Table K). This brings the naphthyl proton HN8 to 2.43 Å from the "equatorial" O2′ atom, which is less than the van der Waals sum of 2.6 Å.[36] This repulsion is reflected in the equatorial angle CN1—Si—O2′ of 113.8 (2) Å, larger than the CN1—Si—O2 equatorial angle of 108.4. (2) Å.

These steric effects for **12** and **13** tend to support a structural displacement toward the TBP. However, the lack of assessment of the presence of unsymmetrical hydrogen bonding supplied by the pyridinium cation, in **12** and **13,** packing effects, and the observance that the phenylsilicate **16**[19] has a structure displaced from the TBP toward the RP of 29.5%, comparable to that for **13,** makes additional interpretation subject to considerable uncertainty.



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Hydrogen Bonding

For all three structures, the nitrogen atoms of the pyridinium cations are located such as to suggest hydrogen bonding interactions between the N—H hydrogen atoms and ring oxygen atoms of the anions.

For the essentially rectangular pyramidal **11,** the hydrogen bond appears to be bifurcated and quite symmetrical with HN—O distances of 2.053 (2) and 2.138 (2) Å for O3′ and O2, respectively. For **12,** the HN—O distances are 1.922 and 2.402 Å for O2 and O1′, respectively, which suggests a stronger hydrogen bonding interaction with O2 which has residual equatorial characteristics. For **13** these Distances are 2.527 (5) and 1.849 (5) Å for O2′ and O1, respectively, which suggests that the hydrogen bond is to the axial O1. The O—O distances for the oxygen atoms involved in the H bonding are similar and have values of 2.345 (3), 2.336 (5), and 2.367 (7) Å for **11, 12,** and **13,** respectively.

Associated with the hydrogen bonds in **11–13,** the Si—O bonds involved suffer an increase, averaging 0.02–0.03 Å compared to the non-hydrogen bonded Si—O bonds. This is expected as electron density is removed from the oxygen atoms and involved in the various hydrogen bonds.

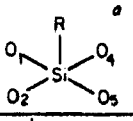
Distortion Coordinate.

As with the isoelectronic phosphoranes, we have shown that the solid-state structures of pentacoordinated anionic silicates provide a range of geometries between the TBP and RP along the Berry pseudorotational coordinate.[4] Here we examine the manner in which "axial" and "equatorial" bond lengths change as one proceeds across the series toward the RP.

The spirocyclic structures of 5–13 provide "axial" and "equatorial" Si—O bond lengths for comparison. These are included in Table V. Several of the structures

TABLE V

Ring Si—O Bond Lengths for Pentacoordinated Anionic Cyclic Silicates



[a]

entry	δ_{24}[e]	Si-O_{ax}[b]	Si-O_{eq}[b]	ref.
5(A)[c]	39.6	(1) 1.792 (5) 1.787		18
5(B)[c]	41.2	(1) 1.806 (5) 1.782		18
6[d]	37.0	(1), (5) 1.794	(2), (4) 1.700	19
7	24.7	(1) 1.769* (5) 1.749*	(2) 1.711 (4) 1.735*	13
8(A)[c]	18.0	(1) 1.742 (5) 1.736	(2) 1.704 (4) 1.706	11
8(B)[c]	26.6	(1) 1.741 (5) 1.738	(2) 1.699 (4) 1.701	11
9	15.3	(1) 1.738* (5) 1.757*	(2) 1.717* (4) 1.685	4
10	5.5	(1) 1.759 (5) 1.753	(2) 1.746 (4) 1.757	4
11	1.2	(1) 1.750* (5) 1.733	(2) 1.734 (4) 1.759*	this work
12	21.9	(1) 1.734 (5) 1.772*	(2) 1.742* (4) 1.722	this work
13	35.5	(1) 1.820* (5) 1.751	(2) 1.71 (4) 1.698	this work

[a] The numbering of the ring oxygen atoms corresponds to that in Table IV. [b] Si-O bond lengths superscripted with an asterisk refer to the involvement of these oxygen atoms in hydrogen bonding. Hydrogen bonding was considered only for X-H···Y distances less than 2.75 Å. [c] Two independent molecules per unit cell. [d] Contains a crystallographic twofold axis colinear with the equatorial phenyl group. [e] The dihedral angle δ_{24} is the one between triangular faces 124 and 245 containing the common equatorial edge 24.

contain one or more of the ring oxygen atoms that are hydrogen bonded. As we discussed, these Si—O bonds are lengthened as a result. Excluding these values, the remainder are plotted in Figure 4 versus the dihedral angle δ_{24}. The latter angle varies from 53.1° to 0° as the structures vary from the TBP to the RP and provides a good measure of the distortion coordinate.[4,37]

While there is considerable scatter, more so for the "axial" bond lengths than the "equatorial" ones, the trends are revealed. As the RP is approached, the difference in bond lengths between the axial and equatorial sets decrease and approach zero. The lines shown are least-squares fits. Essentially the same least-squares equations are obtained if average values of the axial and equatorial Si—O bond lengths are used, one of each type per structure.

From these equations (Figure 4 caption), the Si—O bond lengths for an ideal TBP are calculated to be 1.78 (axial) and 1.68 Å (equatorial). For the RP, the basal Si—O bond length is determined to be 1.73 Å. The axial Si—O bond distance decreases 0.07 Å on forming the RP while the equatorial Si—O bond distance

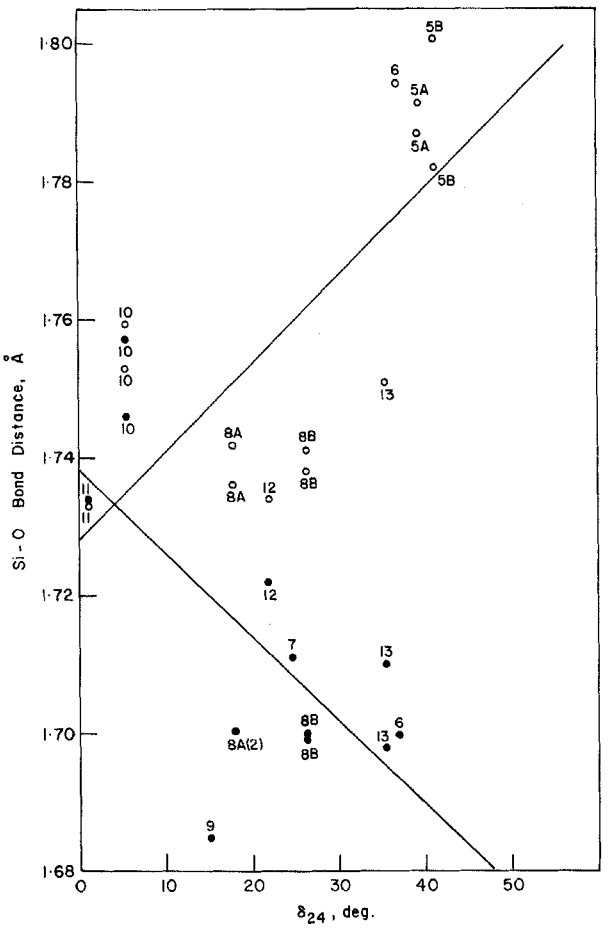


FIGURE 4 Variation of ring Si—O bond lengths for pentacoordinated anionic cyclic silicates vs. the dihedral angle δ_{24}. The numbers refer to compound entries in Table V. The least-squares equation for variation of the "axial" Si—O bond lengths (open circles) is $Si—O_{ax} = 0.001\ 280\delta_{24} + 1.728$; for variation of the "equatorial" Si—O bond lengths (filled circles), $Si—O_{eq} = -0.001\ 202\delta_{24} + 1.738$. The differences in axial and equatorial lengths (Δ) for the non-hydrogen bonded Si—O bonds when plotted vs. δ_{24} give less scatter. The least-squares line for compounds **8, 10, 12,** and **13** is $\Delta = 0.001\ 524\delta_{24} - 0.002\ 907$.

increases by 0.05 Å. For comparison, cyclic phosphoranes containing P—O bonds show a somewhat larger difference between the axial (1.78 Å) and equatorial (1.62 Å) bonds of a TBP, 0.16 Å.[37] For the RP, the basal P—O bond is calculated to be 1.66 Å.[37] Thus, a smaller change is present in the equatorial bonds for phosphoranes (0.04 Å) and a greater change in the axial bond type (0.12 Å) as the RP is reached.

With the assumption that an adequate basis set is at hand, the more equal change in "axial" and "equatorial" Si—O bonds for five-coordinated silicon compounds may imply a greater ease of structural distortion. Since the equatorial bonds in general are stronger,[38,39] their more ready change in length compared to phosphoranes indicates a greater degree of structural nonrigidity. The implication is

that pseudorotational processes, similar to those found for phosphoranes, should exist for pentacoordinated silicon and have ligand exchange activation energies that tend to be not quite as large.

ACKNOWLEDGEMENT

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Registry No. **11,** 88211-66-9; **12,** 88211-68-1; **13** (2-Cl), 88211-70-5; **13** (3-Cl), 88269-15-2; py, 110-86-1; 2,3-dihydroxynaphthalene, 92-44-4; catechol, 120-80-9; phenyltrimethoxysilane, 2996-92-1; 1-naphthyltriethoxysilane, 17938-06-6; (2-chlorophenyl)triethoxysilane, 88211-71-6; (3-chlorophenyl)triethoxysilane, 53392-05-5.

Supplementary Material Available: Table A, anisotropic thermal parameters for **11,** Table B, calculated H atom parameters for **11,** Table C, anisotropic thermal parameters for **12,** Table D, calculated H atom parameters for **12,** Table E, anisotropic thermal parameters for **13,** Table F, calculated H atom parameters for **13,** Table G, additional bond lengths and angles for **11,** Table H, additional bond lengths and angles for **12,** Table I, additional bond lengths and angles for **13,** Table J, deviations from some least-squares mean planes for **11,** Table K, deviations from some least-squares mean planes for **12** Table L, deviations from some least-squares mean planes for **13,** and a listing of observed and calculated structure factor amplitudes (37 pages). Ordering information is given on any current masthead page.

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