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Pentacoordinate Cyanosiliconates

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A study in tetrahydrofuran (THF) solution of the equilibrium process

$$\underset{1}{Bu_4N^+CN^-} + \underset{2}{Me_3SiCN} \rightleftharpoons \underset{3}{Bu_4N^+Me_3Si(CN)_2^-}$$

using IR and ^{29}Si NMR techniques has provided the association constant $K^{24\,°C} = 2.3$ M^{-1} and thermodynamic parameters $\Delta H = -9.0$ kcal/mol, $\Delta S = -28$ eu, and $\Delta G^{24\,°C} = -0.5$ kcal/mol. Tetrabutylammonium dicyanotrimethylsiliconate (**3**) was isolated in crystalline form. IR and FT-Raman analysis of the crystals and FT-Raman analysis of a THF solution of **3** show a CN stretching frequency for **3** in the 2130–2140-cm^{-1} region. Extended basis set ab initio calculations for the model compounds with two axial substituents $H_3Si(CN)_2^-$ (**6a**), $H_3Si(CN)(NC)^-$ (**7a**), and $H_3Si(NC)_2^-$ (**8a**) have found the relative energies (in kcal/mol) for **6a** (0.0), **7a** (1.9), and **8a** (4.0) at the MP-2 level. Structures with one equatorial CN substituent are much higher in energy. The calculated CN vibrational frequencies are in good agreement with the experimental observations in the IR and FT-Raman spectra of trigonal-bipyramidal **3** in the solid and in solution. The IR equatorial CN ν in spirosilane anion **5** (2185 cm^{-1}) and the axial CN ν in cyclic silane anions **4a** (2132 cm^{-1}) and **4b** (2130 cm^{-1}) are in good agreement with the calculated axial and equatorial CN frequencies of **6** and support the assigned structure of **3**. The axial position of the CN group in **4a** was confirmed by X-ray structure analysis. A study of the interaction of cyanide ion with the sterically hindered cyanosilanes, triisopropylsilyl cyanide **11** and tri-*tert*-butoxysilyl cyanide **12**, shows that equilibrium concentrations of these dicyanotrialkylsiliconates are very low. Although cyanide exchange of **11** is fast on the NMR time scale, cyanide exchange of **12** is very slow.

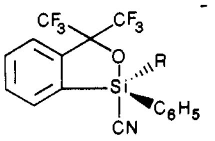
Introduction

Pentacoordinate silicon anions have been implicated as reaction intermediates in numerous processes,[1] and several pentacoordinate siliconates stabilized by chelating ligands on a multiplicity of electronegative substituents have been isolated and characterized.[2] Recently, considerable theoretical attention[3] has been focused on the process of eq 1. Indeed, the prediction has been made that

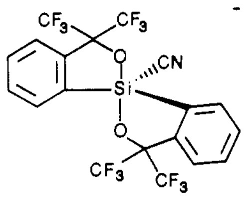
$$R_3SiX + Y^- \rightarrow R_3SiXY^- \quad (R = CH_3, H) \qquad (1)$$

$$\underset{1}{Bu_4N^+CN^-} + \underset{2}{Me_3SiCN} \rightleftharpoons \underset{3}{Bu_4N^+Me_3Si(CN)_2^-} \qquad (2)$$

the stability of such a pentacoordinate siliconate will be greatest when X = Y.[3f] But, with the exception of fluorinated examples,[2a-f] such simple, acyclic pentacoordinate siliconates have resisted isolation and characterization. We wish to report our study of the thermodynamics of the reversible addition of cyanide ion (as tetrabutylammonium cyanide) to trimethylsilyl cyanide (**2**) in tetrahydrofuran (THF) solution and the isolation of tetrabutylammonium dicyanotrimethylsiliconate (**3**) (eq 2). Significantly, formation of dicyanotrimethylsiliconate, as in eq 2, had been postulated[1c] to be responsible for inhibition of cyanide-catalyzed group transfer polymerization of methyl methacrylate initiated by **2** by tying up the polymerization catalyst, cyanide ion. Our study also includes the related cyanosiliconates **4** and **5**, in which



4a, R = Ph
b, R = Me



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we can examine the bonding of CN in both equatorial and axial positions. We have carried out extended basis set ab initio calculations for the model compounds $H_3Si(CN)_2^-$ (**6a,b**), $H_3Si(CN)(NC)^-$ (**7a–c**), and $H_3Si(NC)_2^-$ (**8a,b**) with both CN and NC in axial positions (**a**) or with one axial and one equatorial (**b**, **c**). Good agreement with the spectral data for trigonal-bipyramidal **3–5** is found.

Experimental Section

Materials and Methods. Trimethylsilyl cyanide was purchased from Aldrich Chemical Co., distilled before use, and handled in a drybox under nitrogen. Tetrahydrofuran (THF) was distilled over sodium metal and benzophenone. Anhydrous acetonitrile was purchased from Aldrich Chemical Co. and used without further purification unless otherwise noted. Triisopropylchlorosilane was purchased from Petrarch Systems and used without further purification. Tetrabutylammonium cyanide was purchased from Fluka Chemical Co., dried for 18 h at 10^{-3} Torr, and handled in a drybox. Sodium cyanide-^{13}C (99 atom % ^{13}C) and sodium cyanide-^{15}N (99 atom %) were purchased from Merck Sharp and Dohme Isotopes. Bis[α,α-bis(trifluoromethyl)benzenemethanolato-C^2,O]silicon,[4] [α,α-bis(trifluoromethyl)benzenemethanolato-C^2,O]methylphenylsilicon,[5] and [α,α-bis(trifluoromethyl)benzenemethanolato-C^2,O]diphenylsilicon[6] were prepared by literature methods. Tri-*tert*-butoxysilyl cyanide was prepared as described earlier.[7]

NMR spectra were recorded on a Nicolet NT300WB spectrometer at 59.75 MHz for ^{29}Si, 75.6 MHz for ^{13}C, 30.5 MHz for ^{15}N, and 300.75 MHz for ^{1}H. ^{1}H, ^{13}C, and ^{29}Si spectra were referenced to tetra-

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methylsilane, and ^{15}N was referenced to nitrate of an external saturated aqueous ammonium nitrate solution. ^{29}Si NMR spectra were recorded by using either a gated pulse sequence to suppress the nuclear Overhauser effect or a DEPT pulse sequence[8] with the final proton pulse set to 45° or less, depending on the number of coupled protons, with the delay τ between the pulses set to $0.5J_{SiH}$. FT-Raman spectra were obtained on a Bomem DA 3.02 interferometer operating in the near-infrared region. A Nd/YAG laser (1.064 μm) provided 300 mW of incident power. The laser was focused to a spot approximately 200 μm in diameter, so the power density was not high enough to cause a problem with thermal decomposition. In addition, the lack of an efficient absorption pathway at 1.06 μm minimizes thermal problems. The sensitivity of FT-Raman spectroscopy is now quite comparable to conventional visible Raman spectroscopy using single-channel detection. However, the real advantage behind this approach is the elimination of fluorescent interferences.[9] The systems under study exhibited a high background when examined in the visible region with 5145-Å excitation. The use of a near-infrared laser minimized this problem. The solid-state IR spectrum was obtained on a Nicolet 7199 spectrometer operating with diffuse reflectance, 4-cm^{-1} resolution, and 256 scans. All samples for spectroscopic analysis were prepared in a drybox.

Spectroscopic Determination of Association Constant for Eq 2. The infrared spectrum of a 0.4 M solution of tetrabutylammonium cyanide (**1**) in THF was measured in a 0.1848-mm calcium fluoride IR cell and found to have a molar extinction coefficient (ϵ) of 22.7 L·mol^{-1}·cm^{-1} at 2047 cm^{-1}. A 0.4 M solution of **2** in THF had ϵ 74.3 L·mol^{-1}·cm^{-1} at 2190 cm^{-1}. From the molar extinction coefficients, it was determined that a THF solution nominally 0.4 M in **2** and 0.4 M in **1** was 0.26 M in cyanide and 0.23 M in **2**, the difference in concentrations being due to slight hydrolysis of **2**. This corresponds to a concentration of 0.14 M for the complex, tetrabutylammonium dicyanotrimethylsiliconate (**3**). The ^{29}Si NMR spectrum of a similar solution in THF-d_8 showed, in addition to the resonance at −45.03 ppm, a small amount of hexamethyldisiloxane (δ 7.27) resulting from the estimated 10% hydrolysis of **2**.

Tetrabutylammonium Dicyanotrimethylsiliconate (3). A mixture of 1 mL of 1 M **1** and 1.5 mL of **2** in a 20-mL glass vial was allowed to evaporate in a nitrogen-filled drybox. Crystals formed at the surface of the solution and were periodically broken up since they prevented evaporation of the underlying solution. An amber color gradually formed during the evaporation, which required 3–4 days. The crystals were washed with hexane without apparent change in composition (as judged from the ^{1}H NMR spectrum in acetonitrile-d_3, which showed approximately a 1:1 molar ratio of CH$_2$N, δ 3.15, relative to SiCH$_3$, δ 0.38). Anal. Calcd for $C_{21}H_{45}N_3Si$: C, 68.60; H, 12.34; Si, 7.64. Found: C, 67.70; H, 12.38; Si, 7.73. Storage of the crystals at 0.02 Torr for 18 h or brief washing with diethyl ether led to loss of part of the trimethylsilyl cyanide.

Preparation of Tetraethylammonium Cyanide. To a solution of 100 g of anhydrous tetraethylammonium chloride (dried in a vacuum oven) in 200 mL of anhydrous methanol under a nitrogen atmosphere was added dropwise during 3 h a solution of 50 g of sodium cyanide in 1 L of anhydrous methanol with mechanical stirring. The mixture was filtered under nitrogen, and the filtrate was evaporated with a rotary evaporator. The residue was extracted with 1 L of anhydrous acetonitrile and the solution filtered under nitrogen. The filtrate was concentrated with a rotary evaporator to a volume of 100–200 mL, warmed to obtain a homogeneous solution, and allowed to cool slowly, finally in an ice bath. The crystals of tetraethylammonium cyanide were filtered under nitrogen and dried at 0.1 Torr. The same procedure was followed on a reduced scale to prepare tetraethylammonium cyanide-^{13}C from sodium cyanide-^{13}C (99 atom % ^{13}C) and tetraethylammonium cyanide-^{15}N from sodium cyanide-^{15}N (99 atom %).

Triisopropylsilyl Cyanide.[10] To a stirred solution of 14 g (90 mmol) of tetraethylammonium cyanide in 100 mL of anhydrous acetonitrile was added 11.57 g (12.8 mL, 60 mmol) of triisopropylchlorosilane. After 1 h, the mixture was cooled to −20 °C, and dry ether was added dropwise to cause precipitation of tetraethylammonium chloride. After 50 mL of ether had been added, the mixture was filtered under argon, and the filtrate was evaporated under reduced pressure. The residue was treated with dry ether, the solution filtered under argon, and the filtrate concentrated and distilled in a small spinning band column to give 7.7 g of triisopropylsilyl cyanide: bp 92–93 °C (7.6 Torr); density 0.85 g/mL. ^{1}H NMR (CDCl$_3$, δ): 1.15 (d, J = 5.6 Hz, CH$_3$), 1.1–1.3 (m, CH). GC analysis showed 95% purity. Calcd for $C_{10}H_{21}NSi$: m/z 183.1443. Found: m/z 183.1401.

Tetraethylammonium [α,α-Bis(trifluoromethyl)benzenemethanolato(2−)-C^2,O]cyanodiphenylsiliconate (Et$_4$N-4a). A solution of 948 mg (2.24 mmol) of [α,α-bis(trifluoromethyl)benzenemethanolato-C^2,O]diphenylsilicon[6] in 5 mL of THF was treated with 349 mg (2.24 mmol) of tetraethylammonium cyanide, and the mixture was stirred for 2 h. The solid was filtered out and washed with cold THF. Reprecipitation from acetonitrile–THF–ether gave 1.16 g, mp 171–172 °C. ^{1}H NMR (acetonitrile-d_3, δ): 8.87–8.67 (m, 1 H), 8.00–7.07 (m, 13 H), 3.10 (q, J = 7 Hz, 8 H), 1.12 (t, 12 H). ^{19}F NMR (acetonitrile-d_3–F11, δ): −74.37 (d, J_{HF} = 1.2 Hz). Anal. Calcd for $C_{30}H_{34}N_2F_6OSi$: C, 62.05; H, 5.90; N, 4.82. Found: C, 62.21; H, 6.25; N, 5.27. Crystals for X-ray analysis were grown at −25 °C from an acetonitrile–ether solution. The acetonitrile was purified by distillation over CaH$_2$ and stored over 4-Å molecular sieves. A similar procedure was used for the preparation of [CN-^{13}C]-Et$_4$N-**4a** (99 atom %) and [CN-^{13}C]-Et$_4$N-**5** (99 atom %).

Crystal Structure of Et$_4$N-4a. Crystal data were obtained from a colorless parallelepiped crystal of dimensions 0.19 × 0.30 × 0.48 mm. Data collection was performed with Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 computer-controlled κ-axis diffractometer equipped with a graphite-crystal, incident-beam monochromator. Cell constants and an orientation matrix for data collection were obtained from 20 reflections in the range $8 < \theta < 14°$. The monoclinic cell parameters are a = 9.721 (9) Å, b = 17.690 (7) Å, c = 17.100 (4) Å, β = 103.25 (4)°, V = 2862 (5) Å^3, and Z = 4. From the systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, and from subsequent least-squares refinement, the space group was determined to be $P2_1/c$ (No. 14). The data were collected at a temperature of −30 (1) °C by using the ω–θ scan technique. The scan rate varied from 2 to 5°/min (in ω). Data were collected to a maximum 2θ of 46.0°. A total of 3941 reflections were collected, of which 3423 were unique and not systematically absent. As a check on crystal and electronic stability, three representative reflections were measured every 30 min. The slope of the least-squares plot of intensity versus time was 0 (3) counts/h, which corresponds to a total loss in intensity of 0.1%. An anisotropic decay correction was applied. The correction factors on I ranged from 0.961 to 1.424 with an average value of 0.998. Lorentz and polarization corrections were applied to the data. A secondary extinction correction was applied.[11] The final coefficient, refined in least squares, was −0.0000001 (in absolute units).

The structure was solved by direct methods. With the use of 341 reflections (minimum E of 1.39) and 6011 relationships, a total of 32 phase sets were produced. A total of 12 atoms were located from an E map prepared from the phase set with the following probability statistics: absolute figure of merit = 1.23, residual = 28.80, and ψ_0 = 1.370. The remaining atoms were located in succeeding difference Fourier syntheses. The cyano group of the anion was determined to be carbon-bound by first solving for both possibilities and then examining the thermal factors for the carbon and nitrogen atoms. The results (C-bound group: C, 3.07 Å^2; N, 5.34 Å^2. N-bound group: C, 3.50 Å^2; N, 5.13 Å^2) demonstrate that the species is carbon-bound. Hydrogen atoms were added to the structure factor calculations at their calculated positions, but their positions were not refined. The structure was refined in full-matrix least squares, where the function minimized was $\sum w(|F_o| - |F_c|)$. Unit weights were used for all observed reflections. Neutral-atom scattering factors were taken from Cromer and Waber.[12a] Anomalous dispersion effects were included in F_c;[13] the values for f' and f'' were those of Cromer.[12b] Only the 2800 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 362 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.079$$

$$R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.077$$

The standard deviation of an observation of unit weight was 2.06. All calculations were performed with the program SDP-PLUS.[14]

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Ab Initio Calculations. Ab initio calculations were performed with the programs HONDO[15] on an IBM 3081 and GRADSCF[16] on CRAY-1A and CRAY X-MP/24 computers. Geometries were gradient optimized[17] in D_{3h} symmetry for **6a** and **8a** and in C_{3v} symmetry for **7a**. The structures **6b**, **7b** (CN_{ax}, NC_{eq}), **7c** (CN_{eq}, NC_{ax}), and **8b** were optimized in C_s symmetry. The force fields and IR intensities were calculated analytically[18] at the optimized geometries. The intensity of an infrared transition is proportional to $(\partial\mu/\partial q)^2$, where μ is the dipole moment and q is a normal coordinate. One calculates the dipole moment derivatives as $\partial^2E/\partial F\,\partial Q$, where E is the energy, F is an applied electric field, and Q is a nuclear displacement. Once the second derivatives of the energy with respect to the nuclear coordinates have been calculated (required for force constants), the infrared intensities can be obtained extremely cheaply in terms of computer time. Correlation corrections were determined by perturbation theory at the MP-2 level.[19] The geometry optimizations were done with a polarized double basis set (basis set 1) of the form (11s7p1d/9s5p1d/4s1p)/[6s4p1d/3s2p1d/2s1p] in the order Si/C, N/H.[20] Final calculations at the optimized geometry were done with a larger basis set of the form (13s9p1d/10s6p1d/5s1p)/[6s4p1d/5s3p1d/3s1p][21] (basis set 2). An additional set of calculations of the SCF and MP-2 energies was done by augmenting basis set 2 with diffuse p functions on Si, C, and N and a diffuse s function on H to give basis set 3. The diffuse exponents obtained by scaling are $\xi_p(\mathrm{Si}) = 0.023$, $\xi_p(\mathrm{C}) = 0.0335$, $\xi_p(\mathrm{N}) = 0.0486$, and $\xi_s(\mathrm{H}) = 0.032$. Basis set 3 had 140 basis functions.

Results and Discussion

Spectrometric Detection of 3. Examination of the ^{29}Si NMR spectra of solutions of trimethylsilyl cyanide **2** and tetrabutylammonium cyanide **1** in THF-d_8 reveals a large upfield chemical shift due to substantial concentrations of **3**. A 0.4 M solution of **2** in THF-d_8 shows a single sharp ^{29}Si resonance peak at −11.89 ppm and a ^{13}C CN resonance at 126.86 ppm. In a THF-d_8 solution nominally 0.37 M in **2** and 0.4 M in **1**, however, the ^{29}Si resonance moved upfield to −45.03 ppm (broad), while the ^{13}C CN resonance of **2** at 126.86 ppm and the resonance of **1** at 167.00 ppm were replaced with a single resonance at 146.63 ppm. This is consistent with the equilibrium of eq 2 in which the ^{29}Si resonance and the ^{13}C CN resonance are the time-averaged signals resulting from the rapid (on the NMR time scale) equilibration. To determine the actual concentrations of CN^-, **2**, and **3**, the infrared absorbances of 0.4 M **1** at 2047 cm^{-1} and 0.4 M **2** at 2190 cm^{-1} in THF were compared with those of a solution of both **1** and **2**, nominally 0.4 M in **1** and 0.37 M in **2**. From the reductions in absorbance it was determined that the concentrations were 0.26 M in CN^-, 0.23 M in **2**, and 0.14 M in **3**. No absorption at 2130–2140 cm^{-1} for the asymmetric CN stretch of **3** was observed, consistent with the calculated very small extinction coefficient for this vibration in $H_3Si(CN)_2^-$ (vide infra). From these concentrations, the value of K_1 for eq 2 was calculated to be 2.3 M^{-1} in THF at 24 °C. Using these IR-determined concentrations, we calculate that the ^{29}Si δ for **3** is −138.67, which is about 127 ppm to high field of the δ for **2** and not inconsistent with observations of 100 ppm or more in other systems.[22-24] Likewise, the ^{13}C δ for CN of **3** is calculated to be 141.26.

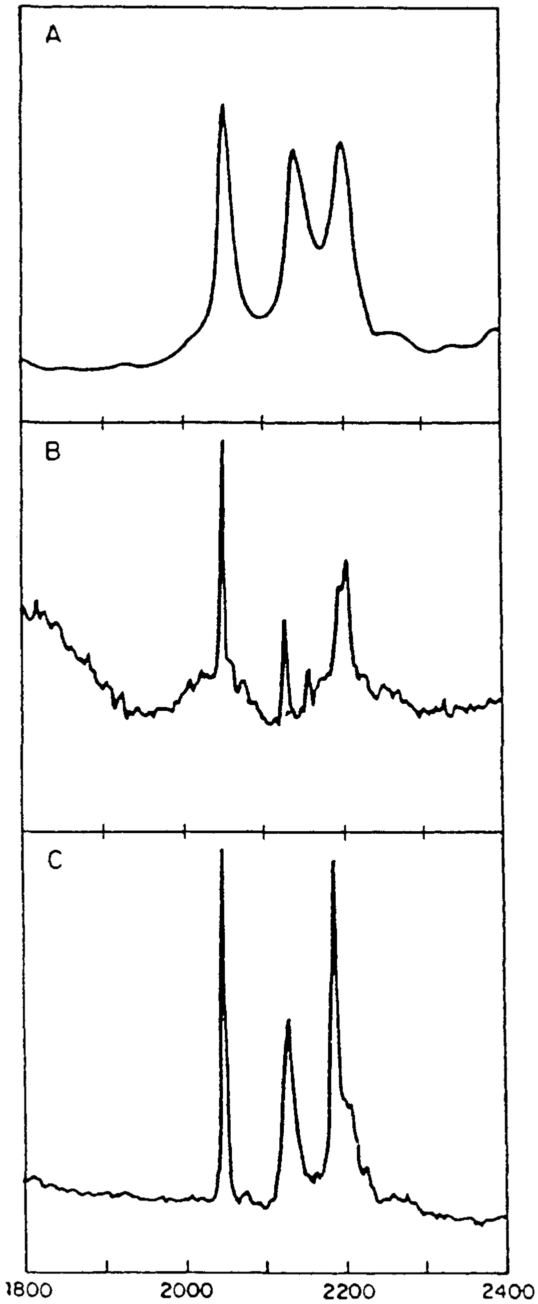

Figure 1. Vibrational spectra for the CN-stretch region: (A) diffuse reflectance infrared spectrum of solid **3**; (B) FT-Raman spectrum of solid **3**; (C) FT-Raman spectrum of the solution of **1** and **2**.

The thermodynamic parameters of the equilibrium of eq 2 were determined by measuring the ^{29}Si δ at 55 °C for the solution of **2** and **1** in THF-d_8 (−31.95). From δ the concentrations were calculated, and the value of K_1 at 55 °C was found to be 0.55 M^{-1}. From the 24 and 55 °C values of K_1 are obtained $\Delta H = -9.0$ kcal/mol, $\Delta S = -28$ eu, and $\Delta G^{24\,°\mathrm{C}} = -0.5 \pm 0.2$ kcal/mol in THF.

Characterization of Tetrabutylammonium Dicyanotrimethylsiliconate (3). Because of the high concentration of **3** in concentrated solutions of **1** and **2**, it is possible to isolate crystalline **3** as the first isolable example of a pentacoordinate siliconate with

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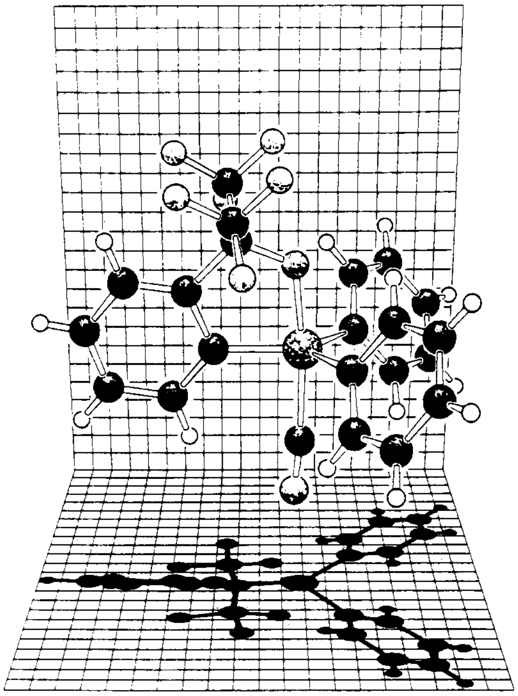


Figure 2. KANVAS perspective drawing of the anion in tetraethylammonium [α,α-bis(trifluoromethyl)benzenemethanolato(2–)-C^2,O]-cyanodiphenylsiliconate.[27]

all carbon-bonded ligands.[25] When a solution of 1 M **1** in acetonitrile was treated with 1.5 volumes of **2** and then allowed to slowly evaporate in an inert atmosphere, crystals of **3** gradually formed. The composition of the crystals was determined by elemental analysis and by ^{1}H NMR spectroscopy in acetonitrile-d_3 solution, which showed 1:1 stoichiometry for the Bu_4N and Me_3SiCN groups. The crystals showed only marginal stability toward dissociation into **2** and **1**. When the crystals were subjected to a pressure of 20 mTorr for 18 h, approximately half of the silicon was removed as **2**. Rinsing of the crystals with ether also removed some of the silicon as **2**. However, washing the crystals with hexane did not appear to disrupt them. An amber color appeared in the evaporating solution during deposition of the crystals due to an unidentified side reaction. Concomitant with the color formation was formation of a paramagnetic impurity (detected by solid-state ESR spectroscopy) that contaminated the crystals and prevented detection of ^{29}Si or ^{13}C NMR signals with magic angle spinning. Thus, we were unable to confirm the assigned ^{29}Si NMR δ of –138.67 for **2**. An X-ray structure could not be obtained because decomposition products within the crystals interfered with their diffraction.

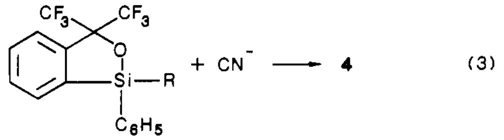
IR and FT-Raman spectroscopies were used for characterization of powdered samples of **3**. The IR spectrum of crystalline **3** between 1900 and 2400 cm^{-1} (the region of the CN stretch) is given in Figure 1A. In Figure 1B, the FT-Raman spectrum of the solid in this region is given, and in Figure 1C, the FT-Raman spectrum of the solution of **1** and **2** (nominally 1 M in each) in this region is shown. The peak near 2200 cm^{-1} (2198, 2199, and 2198 cm^{-1} in Figure 1A–C) corresponds to the CN stretch in **2** (present in equilibrium with **3** even in crystalline samples). The peak near 2050 cm^{-1} (2049, 2050, and 2051 cm^{-1} in Figure 1A–C) corresponds to the CN stretch in **1**. In all three spectra there is a peak near 2130–2140 cm^{-1} (2137, 2128, and 2131 cm^{-1} in Figure 1A–C). We assign this peak to a CN stretch in $Me_3Si(CN)_2^-$. The 2130–2140-cm^{-1} region is not a "normal" region for Si–CN or Si–NC absorptions to occur. Silyl cyanides invariably show IR absorption near 2200 cm^{-1}, while silyl isocyanides invariably show absorption near 2100 cm^{-1}.[26]

Table I. Spectroscopic Features of Silanes and Cyanosiliconates

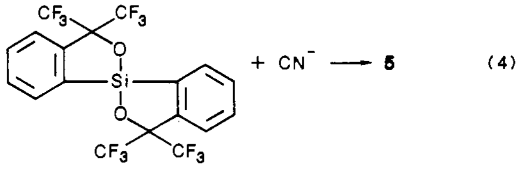
compd	$\delta(^{29}Si)$	$\delta(^{13}CN)$	ν_{CN}, cm^{-1}
4a		145.7^{a,c}	2132 (ϵ 2.2), 2082 (ϵ 8.3)^{a,c}
9a	11.37^{c}		
4b	–80.06^{a,d}	147.26^{a,d}	2130, 2085^{a,e}
9b	25.03^{d}		
5	–91.54^{b,d}	129.98^{b,e}	2185^{a,c} (2183^{a,e})
10	7.89^{f}		
3	[–138.67]^{a,c,g}	[141.26]^{a,c,g}	2131^{a,c,h}
2	–11.89^{c}	126.86^{c}	2190^{c}

^{a} In situ preparation of cyanosiliconate by reaction of stoichiometric quantities of tetraalkylammonium cyanide and silane. ^{b} Solution of preformed cyanosiliconate. ^{c} THF solution. ^{d} Acetonitrile solution. ^{e} Propylene carbonate solution. ^{f} Chloroform solution. ^{g} Brackets indicate values are extrapolated. ^{h} FT-Raman spectroscopy in THF solution.

Pentacoordinate Cyanosiliconates with Bidentate Ligands. To spectroscopically characterize both equatorial and axial cyano groups in pentacoordinate cyanosiliconates, the anions **4a**,[5] **4b**,[5] and **5**[2g] were examined. The pentacoordinate siliconates **4a**, **4b**, and **5** were prepared by reaction of the tetracoordinate silanes **9** and **10** with tetraalkylammonium cyanide (eq 3 and 4).



9a, R = Ph
b, R = Me



10

Et_4N-**4a** was obtained as crystals suitable for X-ray analysis. The trigonal-bipyramidal structure[27] (Figure 2) features an axial cyano group (rather than an isocyano group). IR analysis of a solution in THF of equimolar quantities (0.5 M) of **9a** and **1** showed very weak bands at 2132 cm^{-1} (ϵ 2.2 L·mol^{-1}·cm^{-1}) and 2082 cm^{-1} (ϵ 8.3 L·mol^{-1}·cm^{-1}). A saturated solution of Et_4N-**4a** in THF (only 0.02 M) showed the same IR absorptions. Similar absorption bands were observed in the IR spectrum of a solution of **4b** formed by reaction of equimolar amounts of tetraethylammonium cyanide and **9b** in propylene carbonate solution (2130 cm^{-1} (ϵ ~0.3 L·mol^{-1}·cm^{-1}) and 2085 cm^{-1} (ϵ ~0.8)). The observation of significant isocyanide bands in the IR spectra of Et_4N-**4a** and Et_4N-**4b** at 2082 and 2085 cm^{-1}, respectively, is consistent with the calculated small energy difference (1.9 kcal/mol) between –SiCN and –SiNC in **6a** and **7a** (vide infra). ^{13}C NMR analysis in acetonitrile of Et_4N-**4a** containing 99 atom % ^{13}C enrichment in the cyano group showed a single resonance for the CN at 145.7 ppm, and no ^{29}Si resonance could be detected presumably due to the fortuitous rate of cyanide exchange between silicon and solvent (whether THF or acetonitrile). The related cyanosiliconate Et_4N-**4b** showed a ^{29}Si resonance at –80.06 ppm since the rate of cyanide exchange was apparently much faster than in the case of **4a**.[28] The shielding effect upon the ^{29}Si resonance in going

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(25) Detection of a carbon-bonded pentacoordinate siliconate in the gas phase was reported by: Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480.

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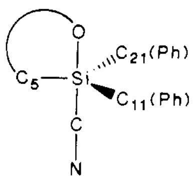
(27) This perspective drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universitat Freiburg, Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours and Co., Wilmington, DE), to produce the back and shadowed planes. The planes bear a 50-pm grid with the lighting source at infinity so the shadow sizes are meaningful.

Table II. Important Structural Parameters for **4a** from the X-ray Analysis[a]



	Distances		
r(Si–O)	1.824 (4)	r(Si–C_{11})	1.902 (5)
r(Si–C)	2.050 (6)	r(Si–C_{21})	1.924 (5)
r(Si–C_5)	1.912 (6)	r(C–N)	1.144 (8)
	Angles		
θ(O–Si–C)	173.4 (2)	θ(C–Si–C_{21})	90.3 (2)
θ(O–Si–C_5)	85.1 (3)	θ(C_5–Si–C_{11})	122.8 (2)
θ(O–Si–C_{11})	94.1 (3)	θ(C_5–Si–C_{21})	126.2 (2)
θ(O–Si–C_{21})	91.9 (3)	θ(C_{11}–Si–C_{21})	111.1 (2)
θ(C–Si–C_5)	88.6 (2)	θ(Si–C–N)	175.1 (4)
θ(C–Si–C_{11})	90.9 (2)		

[a] Bond distances in Å; bond angles in degrees.

from the tetracoordinate **9b** (δ 25.03) to the pentacoordinate cyanosiliconate **4b** is 105.03 ppm. The IR and NMR data are summarized in Table I.

The X-ray structure of **4a** clearly shows a trigonal-bipyramidal structure for the pentavalent anion. Important geometry parameters for the anion are given in Table II, and the remaining data are given as supplementary material. The atoms C_5, Si, C_{11}, and C_{21} form the equatorial plane, with the atoms O and C_N in the axial positions approximately perpendicular to the equatorial plane. Both the angles θ(O–Si–C_N) and θ(Si–C_N–N) deviate somewhat from linearity, by 6.6 and 4.9°, respectively. The Si–C_N axial bond length is significantly longer, 0.13–0.15 Å, than the equatorial Si–C bonds. The C–N bond length is typical of those found for other cyano groups.

The IR spectrum of Bu_4N-**5** (0.5 M in THF), formed from the reaction of equimolar quantities of **1** and **10**, showed absorption at 2185 cm^{-1} (ϵ 1.4 $L \cdot mol^{-1} \cdot cm^{-1}$), and the 2130–2132-$cm^{-1}$ absorptions present in **4b** and **4a** were absent. In the case of **5** the cyano group is necessarily equatorial, and the electronegative oxygen atoms are axial.[4] The ^{29}Si resonance of Et_4N-**5** with 99 atom % ^{13}C in the CN group was a doublet at –91.54 ppm (J_C = 94 Hz), and the ^{13}C CN resonance occurred at 129.98 ppm with silicon satellites (J_{Si} = 94 Hz). There was no trace of a resonance attributable to isocyanosiliconate, so we can conclude that such a species, if present, is less than about 2% in **5**. The ^{29}Si resonance of the spirosilane **10** is at 7.89 ppm in chloroform-*d*–propylene carbonate. Thus, the shielding in forming the pentacoordinate (equatorial) cyanosiliconate is 99.4 ppm.

Interaction of Cyanide Ion with Hindered Cyanosilanes. In order to evaluate the importance of steric and stereoelectronic factors on the rates and equilibria in reactions of cyanide ion with cyanosilanes, the sterically hindered triisopropylsilyl cyanide (**11**)[10] and tri-*tert*-butoxysilyl cyanide[7] were studied (eq 5). Infrared

$$R_3SiCN + CN^- \rightleftharpoons R_3Si(CN)_2^- \qquad (5)$$

11, R = i-Pr
12, R = *t*-BuO

analysis of a solution of **1** and triisopropylsilyl cyanide (**11**) in THF showed no detectable formation of dicyanotriisopropylsiliconate. We conclude, therefore, that the association constant is much smaller than the value of 2.3 M^{-1}, which was determined for **3**.

^{29}Si NMR spectroscopy should be a more sensitive probe than IR spectroscopy for formation of dicyanotriisopropylsiliconate from the interaction of cyanide ion with **11**. The results of examination of the ^{13}C and ^{29}Si NMR spectra of **11** and the related, highly hindered **12**[7] in the presence of tetraethylammonium cyanide are summarized in Table III. The ^{13}C NMR spectrum of **11** and 1 equiv of tetraethylammonium cyanide in acetonitrile showed a single CN resonance that was approximately the average of those of **11** and tetraethylammonium cyanide. This is characteristic of rapid (on the NMR time scale) exchange of CN^- and **11**. However, the ^{29}Si NMR spectrum of **11** showed no shift to higher field upon addition of cyanide ion (Table III, entries 1 and 2). These observations are consistent with the conclusion based on the IR study that the equilibrium constant for formation of dicyanotriisopropylsiliconate is much smaller than that in the case of the reaction of cyanide ion with **2** to give **3**. This is not surprising, since the steric interactions of the isopropyl groups in the transition state leading to the pentacoordinate siliconate are much greater than steric interactions in the transition state for conversion of **2** to **3**.

Table III. ^{13}C and ^{29}Si NMR Data for **11** and **12** in the Presence of Cyanide Ion in Acetonitrile-d_3

entry no.	R_3SiCN and concn, M	concn of Et_4NCN, M	$\delta(^{13}CN)$	$\delta(^{29}Si)$
1	**11** 1.0	0	125.17	5.67
2	**11** 0.45	0.45	144.87	5.58
3	**12** 1.0	0	124.96	–104.48
4	**12**[a] 0.67	0.39	163.60[b] 125.49[c]	–104.48

[a] 20% DMF in $MeCN$-d_3 was used as solvent to minimize precipitation of Et_4NCN by the tri-*tert*-butoxysilyl cyanide. [b] CN^-. [c] SiCN.

In the case of **12**, ^{13}C NMR spectroscopy shows no averaging of the CN signal, and ^{29}Si NMR spectroscopy shows no effect of cyanide ion on the ^{29}Si resonance (Table III, entries 3 and 4). Thus, on the NMR time scale, there is neither exchange with cyanide ion nor formation of dicyanotri-*tert*-butoxysiliconate. Again, this is not surprising in view of the great bulk of the substituents. Electronically, however, formation of the pentacoordinate siliconate should be quite favorable relative to **2**. Clearly, steric factors far outweigh the favorable electronic factors. That cyanide ion exchange with **12** does occur on a slower time scale was demonstrated by the behavior of **12** with 1.0 equiv of tetraethylammonium cyanide-^{15}N (99 atom % ^{15}N in the CN) in 1:1 acetonitrile–DMF. NMR spectroscopy showed that complete equilibration with **12** occurred in less than 3 h. Thus, the ^{15}N spectrum showed two nearly equal resonances at –88.0 and –88.3 ppm, the former corresponding to $C^{15}N^-$ (–87.9 ppm in $Et_4NC^{15}N$), and the latter to **12**-^{15}N. Upon warming of the sample solution, the resonances broadened and moved apart reversibly, indicating that any exchange is very slow on the NMR time scale. The ^{13}C NMR spectrum showed a singlet at 125.55 ppm (**12**-^{14}N), a doublet of about the same intensity at 125.53 ppm (J_N = 12.35 Hz, **12**-^{15}N), a singlet at 166.3 ppm ($C^{14}N^-$), and a doublet at 166.28 (J_N = 5.43 Hz, $C^{15}N^-$). The ^{29}Si NMR spectrum showed a resonance at –104.1 ppm (^{29}Si resonance of **12** occurs at –104.5 ppm). Both the ^{13}C and ^{15}N NMR spectra showed that complete scrambling of the $C^{14}N$ originally present in **12** and the $C^{15}N$ originally present as CN^- had occurred in less than 3 h.

Ab Initio Calculations. Ab initio calculations were performed for $H_3Si(CN)_2^-$ (**6a**), the axial isomers **7a** and **8a**, and the isomers **6b**, **7b**, **7c**, and **8b** with one CN or NC equatorial. The calculated geometry parameters are given in Table IV. The Si–H_{eq} distances are shorter than the Si–H_{ax} bond distances. For the compounds with three H_{eq}'s, the Si–H bond distances are shorter than those with only two equatorial hydrogens. As an axial CN group is substituted by NC, the Si–H_{eq} and Si–H_{ax} bond distances shorten. The CN bond distances are 0.01 Å shorter for the cyanide than for the isocyanide. This difference is smaller than the 0.024-Å difference calculated for SiH_3CN/NC.[7] The Si–C_{ax} and Si–N_{ax} bond distances are 0.20–0.26 Å longer than those calculated for the tetrahedral species, r(Si–C) = 1.872 Å and r(Si–N) = 1.745 Å. Such a bond lengthening for apical substituents in pentavalent structures as compared to the tetrahedral structures is well es-

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(28) The order of relative acceptor strengths, **10** > **9a** > **9b**, was determined by a fluoride ion binding study.

Table IV. Calculated Geometry Parameters for **6**–**8**[a]

property[b]	**6a**	**7a**	**8a**	**6b**	**7b**	**7c**	**8b**
r(C–N)$_{\text{ax}}$	1.150	1.149, 1.159[c]	1.159	1.151	1.151	1.159	1.158
r(C–N)$_{\text{eq}}$				1.145	1.159	1.145	1.158
r(Si–C)$_{\text{ax}}$	2.086	2.067		2.136	2.107		
r(Si–C)$_{\text{eq}}$				1.924		1.923	
r(Si–N)$_{\text{ax}}$		1.958	1.959			2.000	1.980
r(Si–N)$_{\text{eq}}$					1.815		1.810
r(Si–H)$_{\text{ax}}$				1.540	1.533	1.538	1.531
r(Si–H)$_{\text{eq}}$	1.473	1.471	1.468	1.486	1.487	1.480	1.482
θ(Si–C–N(NC))$_{\text{ax}}$	180	180	180	174.5	173.7	175.9	174.4
θ(Si–C–N(NC))$_{\text{eq}}$				175.8	176.4	175.4	175.4
θ(C(N)$_{\text{ax}}$–Si–H$_{\text{ax}}$)				176.3	176.0	175.9	176.3
θ(C(N)$_{\text{ax}}$–Si–H$_{\text{eq}}$)	90	90.0	90	86.1	86.4	86.7	86.8
θ(C(N)$_{\text{eq}}$–Si–H$_{\text{ax}}$)				89.6	89.7	89.3	89.9
θ(C(N)$_{\text{eq}}$–Si–H$_{\text{eq}}$)				119.0	120.1	118.9	119.6
θ(C(N)$_{\text{ax}}$–Si–C(N)$_{\text{eq}}$)				86.6	86.3	86.6	86.4
θ(H$_{\text{ax}}$–Si–H$_{\text{eq}}$)				95.7	95.6	95.2	95.1
θ(H$_{\text{eq}}$–Si–H$_{\text{eq}}$)	120	120.0	120	120.8	118.6	121.2	119.8

[a] Bond distances in Å; bond angles in degrees. [b] For the bond angles, the value not in the internal parentheses corresponds to cyano bonding and the value in the internal parentheses corresponds to isocyano bonding. [c] The first value is for the cyano; the second is for the isocyano.

Table V. Calculated Vibrational Frequencies for **6**–**8**

molecule	ν_1, cm^{-1} [a]	I_1, km/mol[b]	assgnt[c]	ν_2, cm^{-1}	I_2, km/mol	assgnt
6a	2392	0	ax, CN, a_1'	2390	3.1	ax, CN, a_2''
7a	2403	3.0	ax, CN, a_1	2297	151	ax, NC, a_1
8a	2313	438	ax, NC, a_2''	2303	0	ax, NC, a_1'
6b	2443	0.1	eq, CN, a′	2380	2.2	ax, CN, a′
7b	2385	3.9	ax, CN, a′	2323	275	eq, NC, a′
7c	2445	0.3	eq, CN, a′	2315	166	ax, NC, a′
8b	2338	147	eq, NC, a′	2316	292	ax, NC, a′

[a] Calculated harmonic frequency. [b] Calculated infrared intensity. [c] Assignments are by axial or equatorial position, cyano or isocyano bonding, and symmetry type.

tablished.[3,29] The calculated Si–C$_{\text{ax}}$ bond distances are longer than the distance observed in **4a**. The lengthening ranges from 0.04 Å in **6a** to 0.09 Å in **6b**. These differences are due to stereoelectronic differences in the apical substituents. The best "leaving" group is the perfluoroalkoxy group found in **4a** followed by CN$^-$ and by H$^-$. Thus, the shortest Si–C$_{\text{ax}}$ bond is found opposite the best leaving group, **4a**, and the longest is found opposite the worst leaving group, **6b**. The Si–C$_{\text{eq}}$ and Si–N$_{\text{eq}}$ bond distances are closer to the tetrahedral bond lengths, 0.09 Å longer for r(Si–C$_{\text{eq}}$) and 0.07 Å longer for r(Si–N$_{\text{eq}}$).

The structures for **6a**, **7a**, and **8a** have linear NCSi or SiNC bonds as well as linear bonds at Si for the angle ax–Si–ax due to symmetry restrictions. If one group is axial and one equatorial, the SiCN and SiNC bonds clearly deviate from linearity as do the ax–Si–H$_{\text{ax}}$ bond angles. This is just what is found in **4a**, where θ(O–Si–C) = θ(ax–Si–ax) = 173.4° and θ(Si–C–N) = 175.1°. The calculated values for θ(Si–C–N) when CN is axial are 174.5 and 173.7°, which are comparable to the observed value.

The stretching frequencies for the C–N bond are given in Table V. The axial cyano stretching frequencies are about 100 cm^{-1} higher than the frequencies of the axial isocyano stretches, and the equatorial stretching frequencies show a comparable difference. This difference is somewhat smaller than the ~200 cm^{-1} calculated for the CN stretches in SiH$_3$CN/NC.[7] The splitting of 100 cm^{-1} is similar to what is observed experimentally in Me$_3$SiCN/NC.[26a] The symmetric a_1' CN stretch in **6a** is not IR active by symmetry and occurs 2 cm^{-1} above the asymmetric stretch, which is IR active. The asymmetric a_2'' CN stretch has a very low intensity of only 3 km/mol just as found for the CN stretch in SiH$_3$CN, where the IR intensity is predicted to be 11 km/mol.[7] In contrast, the asymmetric a_2'' CN stretch in **8a** occurs at 10 cm^{-1} above the symmetric stretch and is very intense, 438 km/mol. This intensity is similar to the value of 505 km/mol predicted for the CN stretch in SiH$_3$NC.[7] Because of the position of the CN stretch in **8**, it can mix with the symmetric Si–H stretch, which occurs at 2355 cm^{-1}. For **7a**, the cyano CN stretch is predicted to be weak, 3 km/mol, and the isocyano CN stretch is predicted to be quite strong, 151 km/mol. The two CN stretches in **7a** are split by about 100 cm^{-1}. The cyano CN stretch is shifted slightly above the CN stretches in **6a**, and the isocyano CN stretch is shifted slightly below the CN stretches in **8a**. The isocyano stretch mixes with the symmetric Si–H stretch at 2332 cm^{-1}, just as found for the symmetric CN stretch in **8a**. The equatorial CN stretches are shifted above the axial values by 50–60 cm^{-1} for the cyano stretches and by 30–40 cm^{-1} for the isocyano stretches.

We have assigned the peak in the 2130–2140-cm^{-1} region of the FT-Raman and solid IR spectra (Figure 1) of Me$_3$Si(CN)$_2^-$ to a CN stretch. From our calculated value for the CN stretch in **6a** we find that a scale factor of 0.89 is required for agreement with the experimental value for **3**. Such scale factors are required because correlation corrections were neglected and because the calculated frequencies are harmonic whereas the experimental values include anharmonic effects.[30] For comparison, the scale factor for the CN stretch between calculated H$_3$SiCN and experimental Me$_3$SiCN frequencies is 0.88,[7] and the same scale factor is required for other cyano compounds.[7] The CN stretch for **3** in Figure 1A is the asymmetric stretch and in Figure 1B is the symmetric stretch. The difference of the positions for the CN stretch for **3** in Figure 1A,B is larger than the predicted difference for **6a**, but medium effects clearly play a role. The presence of peaks corresponding to **1** and **2** in the vibrational spectra of solid **3** (Figure 1A,B) attests to the inherent instability of crystalline **3**, which readily reverts to **1** and **2**. The bands at 2132 cm^{-1} for **4a** and 2130 cm^{-1} are clearly assigned as the axial CN stretches on the basis of the above analysis. The ab initio calculations predict that the equatorial cyano CN stretch should be 50–60 cm^{-1} higher than the axial cyano CN stretch. Thus, we assign the band at 2183–2185 cm^{-1} in **5** as an equatorial cyano CN stretch.

We have previously shown[7] that correlation corrections are required to obtain the proper sign of the energy difference for SiH$_3$CN/NC. Furthermore, we have also shown[31] that the addition of diffuse functions makes only small changes in the relative energies of isomers and does not change the qualitative results. Examination of Table VI again demonstrates this conclusion. The largest difference in relative energies due to the presence of diffuse functions at the SCF level is 0.7 kcal/mol and at the MP-2 level is 1.3 kcal/mol. For the ions with two axial substituents, **6a** is the least stable and **8a** the most stable at the SCF level. This energy ordering reverses at the MP-2 level (basis set 3), with **6a** being 1.9 kcal/mol more stable than **7a** and 4.0 kcal/mol more

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(29) Dixon, D. A., unpublished results on SiH$_n$F$_{5-n}$ and SiH$_n$F$_{4-n}$.

(30) Dixon, D. A.; Miller, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 3656.

(31) Dixon, D. A.; Smart, B. E.; Fukunaga, T. *J. Phys. Org. Chem.* **1988**, *1*, 153.

Table VI. Relative Energies (kcal/mol) for **6–8**

molecule	ΔE(SCF)[a] basis set 2	ΔE(SCF)[b] basis set 3	ΔE(MP-2)[c] basis set 2	ΔE(MP-2)[d] basis set 3
6a	0.0	0.0	0.0	0.0
7a	−0.7	−1.0	2.5	1.9
8a	−0.9	−1.6	5.2	4.0
6b	13.6	13.7	11.9	11.8
7b	14.6	14.4	18.0	17.3
7c	12.3	12.0	13.5	12.7
8b	13.9	13.3	19.8	18.5

[a] E(SCF) for $H_3Si(CN)_2^-$ −475.407 986 au (basis set 2). [b] E(SCF) for $H_3Si(CN)_2^-$ −475.409 294 au (basis set 3). [c] E(MP-2) for $H_3Si(CN)_2^-$ −476.103 266 au (basis set 2). [d] E(MP-2) for $H_3Si(CN)_2^-$ −476.106 268 au (basis set 3).

stable than **8a**. Making the good approximation that $\Delta\Delta H^{0K} = \Delta\Delta G^{300K}$ for their relative energies, we predict that there are 4.1% of **7a** and 0.2% of **8a** at room temperature relative to the amount of **6a**. We can use the previously obtained values of ΔH and ΔS for eq 2 together with our calculated relative energies to calculate values of $K^{24\,°C} = 1.3 \times 10^{-1}$ M^{-1} for eq 6 and $K^{24\,°C} = 3.6 \times 10^{-3}$ M^{-1} for eq 7.

$$\mathbf{1} + \mathbf{2} \rightleftharpoons Bu_4N^+Me_3Si(CN)(NC)^- \qquad (6)$$

$$\mathbf{1} + \mathbf{2} \rightleftharpoons Bu_4N^+Me_3Si(NC)_2^- \qquad (7)$$

The structures with one axial substituent and one equatorial substituent are clearly less stable than those with two axial substituents. Thus, we did not study structures with two equatorial substituents. The most stable structure with one axial substituent and one equatorial substituent is **6b** with two cyano groups. Structure **6b** is 11.8 kcal/mol less stable than **6a** with two axial cyano groups. Structure **7c** with an axial cyano and an equatorial isocyano substituent is the next most stable structure. The least stable structures are **7b** and **8b** with an axial isocyano substituent. The ions with an isocyano axial substituent and an equatorial substituent are destabilized by ~6 kcal/mol with respect to the ions with an axial cyano substituent and an equatorial substituent; e.g., ΔE(**7b**–**6b**) = 5.5 kcal/mol, and ΔE(**8b**–**7c**) = 5.8 kcal/mol.

Supplementary Material Available: Crystal structure data for Et_4N-**4a**, including tables of atomic positional parameters, general displacement parameters, root-mean-square amplitudes, bond distances, bond angles, torsional angles, and least-squares planes and ORTEP figures and ball and stick diagrams (16 pages). Ordering information is given on any current masthead page.

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Rates and Equilibria of Alkaline-Earth-Metal Complexes with Diaza Crown Ethers in Methanol

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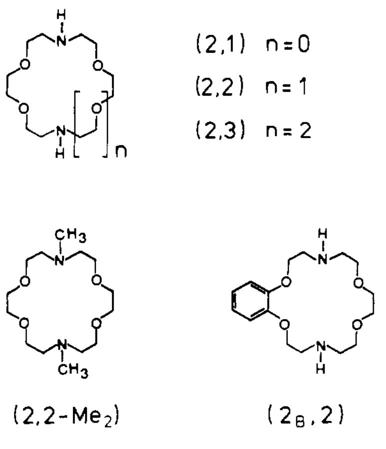
The stability constants and rate constants of formation and dissociation of alkaline earth complexes with a series of diaza crown ethers, (2,1), (2,2), (2_B,2), (2,2-Me_2), and (2,3), in methanol are reported [(2,1) ≡ 1,4,10-trioxa-7,13-diazacyclopentadecane; (2,2) ≡ 1,4,10,13-tetraoxa-6,16-diazacyclooctadecane; (2_B,2) ≡ 2,3-benzo-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane; (2,2-Me_2) ≡ 7,16-dimethyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane; (2,3) ≡ 1,4,7,13,16-pentaoxa-10,19-diazacycloheneicosane]. The diaza crown ethers, like the corresponding fully oxygenated crown ethers, do not show strong selectivity between the alkaline-earth-metal cations Ca^{2+}, Sr^{2+}, and Ba^{2+} or large variations in complex stability with ligand structure and ring size, except when considerable differences between the size of the cation and the ligand cavity are involved. The dissociation rate constants are sufficiently low to allow rate measurements over a range of temperatures with a stopped-flow apparatus. The dissociation reactions of several of the complexes are susceptible to acid catalysis, and those of all nine diaza-18-crown-6 complexes are strongly accelerated by nitrate ions. Complexes of (2,2) and (2_B,2) are up to 7 orders of magnitude less stable than those of the corresponding macrobicyclic cryptands ((2,2,2) and (2_B,2,2), respectively) [(2,2,2) ≡ 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; (2_B,2,2) ≡ 5,6-benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane]. This macrobicyclic or cryptate effect shows up virtually entirely in the dissociation rate constants of the two classes of complexes, with formation rate constants for a given cation being almost identical for mono- and bicyclic ligands.

Introduction

The rate of formation of complexes between alkaline-earth-metal ions and cyclic macromolecular ligands in solution is always several orders of magnitude lower than that of a diffusion-controlled reaction. This means that the dissociation rates of complexes of relatively high stability, such as those of the macrobicyclic cryptand ligands (cryptates),[1] can be followed by conventional techniques, even in water.[2,3] For the less stable, more mobile monocyclic crown ether complexes, it is necessary to use ultrasonic relaxation techniques to determine the complexation kinetics in water.[4] In methanol, however, the stabilities of crown ether complexes are several orders of magnitude higher than those in water with a consequent reduction in the dissociation rate constants. In particular, we have found that for alkaline-earth-metal complexes for diaza-18-crown-6 the dissociation rate constants are sufficiently low to enable rate measurements to be made with a stopped-flow apparatus over a range of temperatures (−10 to +20 °C).[5]

Chart I



(2,2-Me_2) (2_B,2)

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