meric alcohols have slightly different chemical shifts, and the dimethyl sulfoxide was used as an internal standard with a chemical shift of τ 7.48.[17] To determine the relative amounts of α-V and β-V, the singlets for the hydroxyl and methyl protons were integrated. For α- and β-VIII, the singlets for the hydroxyl and for the methyl protons were integrated. When known amounts of the diastereomers were mixed together in different proportions in dimethyl-d_6 sulfoxide, experimental and calculated ratios agreed to within ±1%.

General Procedure for Addition of Ketones to Organometallics. The Grignard reagents were prepared by the usual method in ether. In runs where a different solvent for the reaction was required, the ether was evaporated in the presence of the new solvent in several evaporations. Methyllithium in ether (Foote Mineral Co.) was either used directly, or the ether was displaced with the desired solvent. Phenyllithium in ether (Columbia Organic Chemical Co.) was used directly. In all reactions unless otherwise specified in the footnotes of Tables I and II, the ketones were added to the organometallic solutions while being stirred under dry nitrogen at the desired temperatures. A large excess of organometallic over ketone was employed in all cases. With the hydroxy ketones the excess on a molar basis ranged from 3.1 to 3.0. With the methoxyketones the excess on a molar basis ranged from 4.0 to 0.6. Those reactions conducted at 0 to 35° were carried out for about 70 min and then quenched with water. Reactions carried out at −78° were stirred for about 20 hr before quenching with methanol. In runs 6 and 28 dry cupric sulfate (1 mol/mol of organometallic) was added to the organometallic prior to addition of the ketone. In all runs involving ether, heptane, or benzene as solvent, the reaction mixtures were shaken with water, and the water phase was extracted with ether. The combined organic phases were washed with water, dried, and evaporated. In those runs carried out in 1,2-dimethoxyethane, the reaction mixture was shaken with a mixture of water and methylene chloride, and the organic layer was treated in the usual way. The crude product was subjected to the above chromatographic and analytical procedures.

---

[17] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectral Catalogue," Varian Associates, Palo Alto, Calif., 1962.

Structural Studies of Pentacoordinate Silicon. I. Phenyl-(2,2′,2′′-nitrilotriethoxy)silane

June W. Turley and F. Peter Boer

Contribution from The Dow Chemical Company, Chemical Physics Research Laboratory, Midland, Michigan 48640, and Eastern Research Laboratory, Wayland, Massachusetts 01778. *Received January 31, 1968*

Abstract: The crystal structure of $(C_6H_5)Si(OCH_2CH_2)_3N$ has been determined by three-dimensional X-ray diffraction methods and confirms the predicted pentacoordination of silicon in this compound. The distorted trigonal bipyramid coordination geometry of the silicon has the three equatorial oxygens bent away from the phenyl group toward the nitrogen as shown by the average C–Si–O angle of 97.1° and the average O–Si–O angle of 118.5°. Bond distances to the silicon are Si–O(1) 1.638 Å, Si–O(2) 1.664 Å, Si–O(3) 1.665 Å, Si–C 1.882 Å, and Si–N 2.193 Å. The space group is Pbca with $a = 13.220$ Å, $b = 18.524$ Å, $c = 10.050$ Å and eight molecules per unit cell. The structure was solved by iterative application of Sayre's method in three dimensions using a visual data set. Refinement was by full matrix least squares to a final reliability index of 10.8%.

The existence of pentacoordinate silicon has been postulated for some time. Compounds of such extracoordinate silicon have been proposed as intermediates in the theory of organosilicon reactions,[1] and there has been evidence for pentacoordinate silicon in some stable organic[2-6] and inorganic[7] ions. Stable, easily isolated nitrilotriethoxysilanes, $XSi(OCH_2CH_2)_3N$, have been synthesized,[8-10] and subsequent dipole moment, infrared, neutralization, and solute association studies[10,11] have strongly indicated pentacoordinate silicon in these compounds. A recently published investigation of the crystal structure of dimethylsilylamine pentamer[12] has provided evidence for pentacoordinated Si in that compound. However, the inherent difficulty of locating hydrogen atoms with X-ray diffraction data prevented this study from providing the complete geometry for the coordination.

The determination of the crystal structure of phenyl-(2,2′,2′′-nitrilotriethoxy)silane was undertaken to provide direct evidence for or against the existence of a transannular dative bond between nitrogen and silicon such as would be required by the postulated bonding, and to allow a thorough analysis of the geometry of the Si atom coordination in this compound. It is also interesting to note that, of 13 nitrilotriethoxysilanes tested for biological activity, only the phenyl derivative gave significant results[11] showing high activity with respect to the central nervous system in several species.

Experimental Section

Data Collection. Crystals of phenyl-(2,2′,2′′-nitrilotriethoxy)silane are colorless with a lath-like habit and a melting point of 207–

---

[1] J. R. Chippenfield and R. M. Prince, *J. Chem. Soc., A*, 3567 (1963).

[2] J. Y. Corey and R. West, *J. Am. Chem. Soc.*, **85**, 4034 (1963).

[3] L. H. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[4] C. L. Frye, *J. Am. Chem. Soc.*, **86**, 3170 (1964).

[5] C. L. Frye, G. A. Vincent, and G. L. Hauschildt, *ibid.*, **88**, 2727 (1966).

[6] D. I. Cook, R. Fields, M. Green, R. N. Haszeldine, B. R. Iles, A. Jones, and M. J. Newlands, *J. Chem. Soc., A*, 887 (1966).

[7] B. J. Aylett and J. M. Campbell, *Chem. Commun.*, 159 (1967).

[8] A. B. Finestone, U. S. Patent 3,113,108 (1964).

[9] C. M. Samour, U. S. Patent 3,118,921 (1964).

[10] C. L. Frye, G. E. Vogel, and T. A. Hall, *J. Am. Chem. Soc.*, **83**, 996 (1961).

[11] M. G. Voronkov, *Pure Appl. Chem.*, **13**, 35 (1966).

[12] R. Rudman, W. C. Hamilton, S. Novick, and T. D. Goldfarb, *J. Am. Chem. Soc.*, **89**, 5157 (1967).

208°. X-Ray powder diffraction data were taken with crystal monochromatized Cu Kα_1 radiation (1.54050 Å) on an AEG (Allgemeine Elektrizitäts-Gesellschaft) Guinier camera using Seeman-Bohlin focusing.[13] A 7.5-μ Al foil used as the sample holder provided reference lines. Initial unit cell dimensions obtained from Weissenberg photographs were refined by the method of axial ratios,[14] using the powder data. The lattice parameters of the orthorhombic cell, $a = 13.220 \pm 0.015$, $b = 18.524 \pm 0.008$, and $c = 10.050 \pm 0.001$ Å, give a calculated density of 1.353 g cm^{-3} for $Z = 8$. The space group Pbca was established by the absence of $0kl$ reflections for k odd, $h0l$ for l odd, and $hk0$ for h odd.

A single crystal, approximately 0.4 × 0.2 mm in cross section, was mounted along the long direction and multiple-film packs (Kodak No-Screen medical X-ray film) and Ni-filtered Cu Kα radiation (1.5418 Å) were used on a Weissenberg camera to collect layers $hk0$ through $hk7$, $0kl$, and $1kl$. Intensities were estimated visually by comparison to a scale made from timed exposures of a representative reflection. The intensities were then correlated to a single scale within each film pack and assigned an error $\sigma(F^2) = 0.10F^2$. Next, the different levels were correlated to a single relative scale using intersecting data. For reflections measured on both axes, an average $\overline{F^2} = \sqrt{F_1{}^2F_2{}^2}$ was calculated, with $\sigma(\overline{F^2})$ taken as $(1/\sqrt{2})(0.10\overline{F^2})$ if $F_1{}^2$ and $F_2{}^2$ agreed well, and as $\sqrt{2}\cdot(0.10\overline{F^2})$ if they did not. These σ's were used to compute the weights $w = 2F/\sigma(F^2)$ used in the least-squares refinement, where the quantity $\Sigma w(F_o - F_c)^2$ was minimized. Absolute scale and overall temperature factors were computed by Wilson's method. During the structure refinement a group of 37 reflections appeared to be responsible for delaying convergence in the least-squares iteration, and a check of the raw data showed that all were read at the extreme limits of the intensity scale and were therefore subject to large errors. These 37 reflections were subsequently omitted from the least-squares procedure.

Structure Determination. The structure was solved by iterative application of Sayre's equation[15] in three dimensions. This equation is

$$s(E_a) = s\Big(\sum_{a=b+c} E_bE_c\Big)$$

where s means "sign of," a, b, c are the vectors (hkl) for the reflections a, b, c, and E_a, E_b, and E_c are normalized structure factors for a, b, c. Input to the computer program[16] comprised a set of 236 reflections having $|E| \geqslant 1.5$ and coded instructions which (1) caused this set to be ordered on decreasing size of $|\Sigma^*E|$ where Σ is the sum in Sayre's equation, (2) specified the origin by checking the parity of and assigning positive phases to the first three reflections in the ordered set, (3) allowed the phases of the next four reflections to be either positive or negative resulting in $2^4 = 16$ starting sets of seven phases each (see Table I), and (4) applied Sayre's relation iteratively for each set until no new additions were made to the list of determined phases or until 17 cycles had been done, whichever occurred first. Listed output for each starting phase-set included the set number, hkl, and E for the starting set, and a table of cycle number, number of additional phases determined, number changed, number undetermined, number positive, number negative, and the predicted phases of the starting set for each cycle. Following this was a listing of the total data set with final predicted phases. At the end of the list, the consistency index, C, for the solution was printed. It is this index where the sums are over all pairs of b and c for which

$$C = \frac{\langle |E_a \sum_{a=b+c} E_bE_c| \rangle}{\langle |E_a| \sum_{a=b+c} |E_b||E_c| \rangle}$$

$b + c = a$ and where the average is over all values of a, which is used to indicate which of the generated solutions is most likely to be the true one. Table II shows the results for this structure. The last two columns give the starting phases for the four symbolic phases being cycled, and the predicted phases for these four after the last cycle. Solutions 3 and 11 correspond to 14 except for an origin shift of $^1/_2{}^1/_20$, and solutions 6 and 16 are found to be identical with 14 as is suggested by the fact that the iteration gives predicted phases for the starting sets of solutions 6 and 16 which are the same as the solution 14 starting set. There are no predicted phase changes for the starting set which gave solution 14. The E map calculated from it showed the expected chemical structure clearly except for the carbon atoms bonded to nitrogen. The calculated electron density in this region of the map appeared to indicate a disorder in the positions of these three atoms (see Figure 1) each of which seemed to appear at two different locations approximately 1.0 Å apart as peaks of roughly half normal height. These positions, C(1)′, C(1)″, C(2)′, C(2)″, C(3)′, and C(3)″, were later assumed to be only partially occupied and were treated in the final refinement as independent atoms of weight one-half.

Table I. Starting Set for Application of Sayre's Relation

h	k	l	E
1	2	7	+3.41
9	7	1	+3.34
4	2	3	+2.18
1	10	1	±2.87
1	6	7	±3.25
1	14	1	±3.43
11	2	1	±3.21

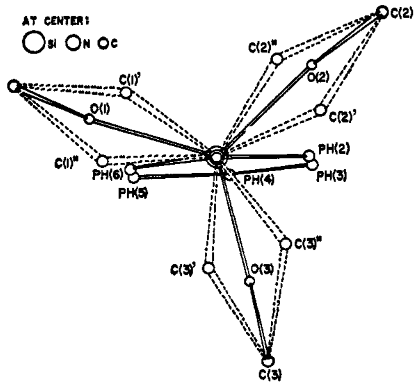

Figure 1. Projection of the phenyl-(2,2′,2″-nitrilotriethoxy)silane structure viewed down the N–Si–PH(1) axis.

Table II. Consistency Indices for Cycled Phase Sets

Set	Cycles	No. +	No. −	C^a	Initial	Predicted
1	17	114	121	0.37236	++++	++++
2	8	119	114	0.48834	+++−	+++−
3	6	110	126	0.87395	++−+	++−+
4	17	124	107	0.59011	++−−	+−−−
5	12	113	120	0.54790	+−++	+−−+
6	6	120	116	0.87954	+−+−	−−+−
7	10	111	119	0.58547	+−−+	+−−+
8	11	115	117	0.42885	+−−−	+−−−
9	17	108	122	0.34507	−+++	−+++
10	8	117	116	0.56729	−++−	−++−
11	10	110	126	0.82208	−+−+	++−+
12	11	115	111	0.52315	−+−−	−+−−
13	14	119	112	0.53493	−−++	−−++
14	6	120	116	0.93297	−−+−	−−+−
15	12	113	120	0.54097	−−−+	+−−+
16	6	120	116	0.88662	−−−−	−−+−

^{a} C = consistency index.

Structure Refinement. Several attempts were made to refine[17] an ordered model having only three of the above six C positions

---

[13] E. Hofmann and H. Jagodzinski, *Z. Metallk.*, **46**, 601 (1955).

[14] L. K. Frevel, *Acta Cryst.*, **17**, 907 (1964).

[15] D. Sayre, *ibid.*, **5**, 60 (1952).

[16] R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1965.

[17] All least-squares refinements were calculated using atomic scattering factors from "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–209.

Table III. Final Atomic Parameters[a]

	Atomic coordinates			Anisotropic thermal displacements, Å[b]					
Atom	x	y	z	$U_{11}^{1/2}$	$U_{22}^{1/2}$	$U_{33}^{1/2}$	$U_{12}^{1/2}$	$U_{13}^{1/2}$	$U_{23}^{1/2}$
C(1)′	0.40744 (89)	0.33624 (84)	0.33700 (153)	0.216 (13)	0.289 (17)	0.211 (24)	0.132 (22)	0.166 (17)	−0.096 (32)
C(1)′′	0.37927 (214)	0.30887 (137)	0.26743 (195)	0.428 (26)	0.394 (24)	0.255 (31)	0.353 (25)	0.276 (25)	0.205 (27)
C(2)′	0.27862 (93)	0.35125 (83)	0.16345 (109)	0.223 (13)	0.307 (14)	0.148 (21)	−0.083 (40)	−0.020 (108)	−0.101 (26)
C(2)′′	0.27023 (182)	0.40468 (158)	0.15896 (243)	0.333 (23)	0.457 (27)	0.364 (23)	0.272 (35)	0.245 (26)	0.228 (38)
C(3)′	0.35192 (155)	0.45739 (96)	0.26356 (139)	0.336 (17)	0.322 (16)	0.041 (83)	−0.175 (26)	−0.064 (52)	−0.088 (36)
C(3)′′	0.39108 (167)	0.44225 (115)	0.32193 (195)	0.347 (22)	0.356 (21)	0.224 (31)	−0.295 (22)	0.162 (30)	−0.176 (27)
C(1)	0.36212 (56)	0.27569 (38)	0.40673 (71)	0.263 (8)	0.279 (9)	0.302 (9)	0.175 (10)	0.163 (10)	0.105 (15)
C(2)	0.16666 (64)	0.37277 (51)	0.16748 (73)	0.271 (8)	0.385 (10)	0.229 (11)	−0.105 (22)	0.067 (25)	0.082 (22)
C(3)	0.33645 (60)	0.48928 (36)	0.40485 (75)	0.305 (8)	0.246 (8)	0.307 (9)	−0.157 (12)	0.188 (10)	−0.146 (11)
ϕ(1)	0.11310 (44)	0.37203 (29)	0.56923 (47)	0.243 (6)	0.246 (6)	0.171 (10)	0.045 (28)	−0.020 (52)	−0.049 (18)
ϕ(2)	0.02323 (50)	0.40776 (31)	0.55562 (49)	0.242 (7)	0.249 (7)	0.222 (8)	0.046 (30)	−0.040 (25)	0.037 (27)
ϕ(3)	−0.04922 (51)	0.41079 (37)	0.65849 (63)	0.243 (7)	0.277 (8)	0.241 (9)	−0.073 (22)	−0.050 (26)	−0.103 (13)
ϕ(4)	−0.03493 (54)	0.37601 (38)	0.77527 (70)	0.263 (8)	0.284 (8)	0.259 (9)	−0.119 (16)	0.177 (8)	−0.102 (16)
ϕ(5)	0.05451 (66)	0.33674 (35)	0.79370 (51)	0.328 (9)	0.285 (8)	0.163 (11)	−0.089 (21)	0.135 (11)	0.085 (15)
ϕ(6)	0.12740 (56)	0.33423 (33)	0.69270 (51)	0.280 (7)	0.275 (7)	0.178 (10)	0.105 (15)	0.094 (13)	0.110 (10)
Si	0.21311 (11)	0.37401 (8)	0.43623 (14)	0.214 (2)	0.228 (2)	0.195 (3)	0.059 (5)	0.045 (6)	0.035 (7)
O(1)	0.27803 (31)	0.30277 (22)	0.48072 (43)	0.246 (6)	0.253 (5)	0.274 (5)	0.107 (10)	0.130 (7)	0.111 (9)
O(2)	0.13437 (34)	0.36616 (31)	0.30803 (43)	0.221 (5)	0.378 (6)	0.236 (7)	−0.010 (140)	−0.026 (40)	0.063 (19)
O(3)	0.25701 (37)	0.45562 (23)	0.47388 (41)	0.272 (5)	0.256 (6)	0.273 (5)	−0.115 (10)	0.132 (8)	−0.103 (9)
N	0.32834 (38)	0.38048 (26)	0.27990 (44)	0.222 (6)	0.250 (6)	0.233 (7)	−0.032 (36)	0.067 (13)	0.062 (15)

[a] The symbol ϕ refers to carbon atoms in the phenyl ring. Numbers in parentheses are the estimated standard deviations from the least-squares refinement × 10^5 for atomic coordinates and × 10^3 for thermal parameters. [b] These values are the square roots of the mean-square-amplitude tensors, U_{ij}, based on the expression $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$ and the relation, *e.g.*, $\beta_{12} = 2\pi^2 U_{12} \cdot a^*b^*$ (D. W. J. Cruickshank, *Acta Cryst.*, **19**, 153 (1965)).

occupied. These failed to refine below $R = 0.22$, and gave unreasonably high thermal parameters at the chosen sites. In addition, electron density maps calculated from phases based on these ordered models invariably gave substantial peaks at the sites left unoccupied. From this evidence, the disordered model described above was assumed to be reasonably correct and refinement proceeded with several cycles of isotropic refinement, giving an over-all reliability index of $R_1 = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.18$. After anisotropic refinement of the ordered atoms concurrent with x, y, z refinement of the disordered atoms, holding their isotropic B's constant, R_1 was reduced to 0.15. At this point, a careful survey of the data set showed a group of 37 reflections for which agreement of F_o and F_c was several orders worse than for the bulk of the data. As previously noted, these reflections were withheld from subsequent refinement. At the same time, a check on the internal correlation of the data showed a need for rescaling, and this was done. Calculations continued with a return to isotropic refinement of all atoms giving $R_1 = 0.16$ and $R_2 = \{\Sigma w[F_o - F_c]^2/\Sigma w F_o^2\}^{1/2} = 0.24$. The thermal parameters, B, for the six positions of the three disordered atoms were 3.85, 7.44, 4.08, 8.96, 4.34, and 5.86 for C(1)′, C(1)′′, C(2)′, C(2)′′, C(3)′ and C(3)′′, respectively, which suggest that the three carbon atoms may occupy the primed positions in more than half of the molecules in the crystal. Two more cycles of anisotropic refinement on all but the disordered atoms gave $R_1 = 0.12$ and $R_2 = 0.18$. Finally, three cycles of anisotropic refinement on all atoms reduced these values to $R_1 = 0.108$ and $R_2 = 0.158$.[18] The average x, y, z, parameter shift for all but the disordered atoms was 0.1σ in the final cycle, with a maximum shift of 0.2σ. For the disordered carbons the average shift was 0.5σ. No hydrogen atoms were included for this structure. Evidence for the presence of hydrogens on the phenyl group was seen in the final difference map, but the expected disorder for those on the ethoxy bridges together with the limitations of the data set precluded their appearance. Atomic parameters and their estimated standard deviations are listed in Table III. Figure 2 is a computer-produced[19] stereo view of the structure in which atoms are represented by ellipsoids corresponding to their final anisotropic thermal parameters. For clarity, simple spheres are used to represent the disordered atoms. Bond distances and angles and their estimated standard deviations, as calculated from the least-squares variance–covariance matrix in the last cycle of refinement, are given in Table IV.

Discussion

The molecular geometry about the silicon atom can be described as a distorted trigonal bipyramid, in which the three oxygens at the equator are bent somewhat away from the phenyl group and toward the nitrogen, as measured by the average C–Si–O angle of 97.1°. This value is considerably nearer to the 90° angle of an ideal trigonal bipyramid than to the value of 109.5° to be expected for tetrahedral silicon. The atoms N–Si–C are essentially collinear as seen from the average deviation of 0.016 Å from the least-squares line through these atoms (defined by the parametric equations $\{x = 0.2182 - 0.0528t;\ y = 0.3755 - 0.0021t;\ z = 0.4285 + 0.0710t\}$). The O–Si–O bond angles show approximately threefold symmetry about this axis with an average value of 118.5°. The silicon atom lies 0.204 Å from the plane[20] $(-9.135x - 0.931y + 7.257z = 0.667)$ of the three oxygen atoms and on the phenyl side. The N–Si–C axis forms an angle of 89.1 ± 0.3° with this plane, essentially perpendicular within 3σ.

The existence of a transannular $\overset{-}{\text{Si}}\leftarrow\text{N}^+$ bond is confirmed by the experimental distance of 2.193 ± 0.005 Å, much shorter than the sum of the respective van der Waals radii, about 3.5 Å. This result is particularly significant since Voronkov[11] has suggested from examination of tetrahedral models that 2,2′,2′′-nitrilotriethoxysilanes can take on a nonstrained "biconvex" structure that excludes any Si–N interaction, as well as the slightly strained "concavo-convex" configuration confirmed in this study. Our bond length is nevertheless somewhat longer than the values (1.94–2.09 Å) recently reported[12] for pentacoordinate Si–N bonds in dimethylsilylamine pentamer, and substantially longer than the range[21–23] of about 1.7–1.8 Å reported for Si–N

---

(18) A table of observed and calculated structure factors has been deposited with the U. S. Library of Congress as Document No. 9868. A copy may be had by citing the document number and remitting $1.25 for microfilm or $1.25 for photoprints to: Photoduplication Service, Library of Congress, Washington, D. C. 20540. Make checks payable to: Photoduplication Service, Library of Congress.

(19) C. K. Johnson, U. S. Atomic Energy Commission Report ORNL-3794, 1965.

(20) J. Gvildys, Argonne National Laboratory, Program Library B-125, 1965; see V. Shomaker, J. Wasser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, **12**, 600 (1959).

(21) M. Yokoi and K. Yamasaki, *J. Am. Chem. Soc.*, **75**, 4139 (1953).

(22) K. Hedberg, *ibid.*, **77**, 6491 (1955).

(23) G. S. Smith and L. E. Alexander, *Acta Cryst.*, **16**, 1015 (1963).

Table IV. Bond Distances and Angles

Bond	Distances, Å	Angles	Deg	Angles	Deg
		In Ethoxy Bridges		With the N-Si-C Axis	
C(1)′-C(1)″	0.942 (29)	N-C(1)′-C(1)	109.36 (53)	O(1)-Si-N	82.88 (19)
C(2)′-C(2)″	0.998 (28)	N-C(2)′-C(2)	108.61 (52)	O(2)-Si-N	83.31 (21)
C(3)′-C(3)″	0.832 (24)	N-C(3)′-C(3)	103.85 (56)	O(3)-Si-N	82.60 (20)
N-C(1)′	1.448 (15)	N-C(1)″-C(1)	102.20 (55)	O(1)-Si-ϕ(1)	99.10 (22)
N-C(2)′	1.449 (12)	N-C(2)″-C(2)	107.63 (60)	O(2)-Si-ϕ(1)	96.32 (23)
N-C(3)′	1.469 (17)	N-C(3)″-C(3)	111.26 (54)	O(3)-Si-ϕ(1)	95.79 (22)
N-C(1)″	1.494 (17)	C(1)′-C(1)-O(1)	107.50 (49)	C(1)′-N-Si	100.73 (61)
N-C(2)″	1.508 (24)	C(2)′-C(2)-O(2)	106.36 (50)	C(2)′-N-Si	104.14 (57)
N-C(3)″	1.476 (14)	C(3)′-C(3)-O(3)	112.43 (52)	C(3)′-N-Si	106.31 (82)
C(1)′-C(1)	1.453 (17)	C(1)″-C(1)-O(1)	116.49 (58)	C(1)″-N-Si	108.94 (90)
C(2)′-C(2)	1.534 (16)	C(2)″-C(2)-O(2)	110.58 (58)	C(2)″-N-Si	103.95 (81)
C(3)′-C(3)	1.553 (18)	C(3)″-C(3)-O(3)	113.67 (53)	C(3)″-N-Si	103.14 (78)
C(1)″-C(1)	1.548 (20)	C(1)-O(1)-Si	123.28 (35)	About the N-Si-C Axis	
C(2)″-C(2)	1.494 (29)	C(2)-O(2)-Si	123.52 (30)	C(1)′-N-C(2)′	115.88 (86)
C(3)″-C(3)	1.406 (23)	C(3)-O(3)-Si	123.50 (28)	C(2)′-N-C(3)′	111.66 (86)
C(1)-O(1)	1.429 (7)	In the Phenyl Ring		C(3)′-N-C(1)′	116.18 (103)
C(2)-O(2)	1.482 (9)	ϕ(1)-ϕ(2)-ϕ(3)	122.39 (49)	C(1)″-N-C(2)″	115.24 (148)
C(3)-O(3)	1.406 (8)	ϕ(2)-ϕ(3)-ϕ(4)	121.52 (63)	C(2)″-N-C(3)″	106.66 (160)
O(1)-Si	1.638 (4)	ϕ(3)-ϕ(4)-ϕ(5)	118.70 (53)	C(3)″-N-C(1)″	117.42 (182)
O(2)-Si	1.664 (5)	ϕ(4)-ϕ(5)-ϕ(6)	120.12 (51)	O(1)-Si-O(2)	117.99 (27)
O(3)-Si	1.665 (4)	ϕ(5)-ϕ(6)-ϕ(1)	121.31 (65)	O(2)-Si-O(3)	118.30 (28)
N-Si	2.193 (5)	ϕ(6)-ϕ(1)-ϕ(2)	115.89 (52)	O(3)-Si-O(1)	119.24 (26)
ϕ(1)-Si	1.882 (6)	N-Si-ϕ(1)	177.90 (22)		
ϕ(1)-ϕ(2)	1.368 (8)				
ϕ(2)-ϕ(3)	1.411 (9)				
ϕ(3)-ϕ(4)	1.354 (10)				
ϕ(4)-ϕ(5)	1.401 (11)				
ϕ(5)-ϕ(6)	1.401 (9)				
ϕ(6)-ϕ(1)	1.439 (8)				

bonds to tetrahedral silicon. Taken together with the measurable distortion of the structure from an ideal trigonal bipyramid, this result suggests that the Si atom is not fully hybridized as sp^3d.

The observed Si-O distances (1.638, 1.664, and 1.665 Å) fall at the high end but within the range of values (1.61-1.67) reported[24-29] for tetrahedral bonds. However, the σ's associated with these reported values are so large that a meaningful comparison cannot be made for the purpose of showing whether or not lengthening of the Si-O bonds occurs in our structure. On the other hand, our Si-C distance of 1.883 Å is significantly longer than the value of 1.843 ± 0.005 Å obtained by electron diffraction[30] for the tetrahedral Si-C bond in phenylsilane.

The bond angles formed by the ethoxy bridges give some insight into the nature of the forces affecting the Si-N bond. The average C-N-Si angle of 104.5° is only slightly flattened from tetrahedral, while the average N-C-C and C-C-O angles, 107.2 and 111.1°, respectively, are also close to tetrahedral values. However, the Si-O-C angles are distorted from the value of 113° found for oxygen bonded to tetrahedral silicon[26] to the average value of 123.4° found here. This result suggests that the disruptive effect of distorting the ethoxy bridges and the stabilizing effect of Si-N bond formation are the major influences in determining the Si-N bond length. Preliminary studies in these laboratories of the structures of nitrilotriphenoxysilanes, where sp^2 hybridization at C constrains the bridge atoms to a rigid planar structure, indicate a substantially longer Si-N bond distance.

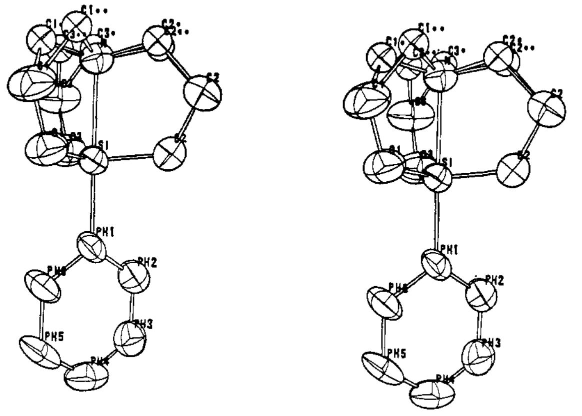

Figure 2. A stereo view of the molecular structure and thermal ellipsoids of phenyl-(2,2′,2″-nitrilotriethoxy)silane with 0.2-Å spheres used for disordered atoms.

As mentioned earlier, the structure was refined on the basis of a model assuming that two possible nonplanar conformations are available to the five-membered rings, and that only the positions of the three C atoms bonded to nitrogen are affected significantly by this disorder. The normal amplitudes of thermal vibration for the other ring atoms support this assumption. For steric reasons, we expect transitions between these conformations to be concerted for all three five-membered rings of a given molecule, *i.e.*, C(1)′-C(2)′-C(3)′, C(1)″-C(2)″-C(3)″. Evidence that such transitions occur rapidly in solution is obtained from the nmr spectrum[11] in which the two NCH_2 protons, and likewise

[24] W. L. Roth and D. Harker, *Acta Crypt.*, **1**, 34 (1948).

[25] E. H. Aggarwal and S. H. Bauer, *J. Chem. Phys.*, **18**, 42 (1950).

[26] K. Yamasaki, A. Kotera, M. Yokoi, and Y. Ueda, *ibid.*, **18**, 1414 (1950).

[27] G. Pyronel, *Atti Accad. Naz. Lincei, Rend. Classe Sci. Fis. Mat. Nat.*, **16**, 231 (1954).

[28] H. Steinfink, B. Post, and I. Fankuchen, *Acta Cryst.*, **8**, 420 (1955).

[29] M. Yokoi, *Bull. Chem. Soc. Japan*, **30**, 100 (1957).

[30] F. A. Keidel and S. H. Bauer, *J. Chem. Phys.*, **25**, 1218 (1956).

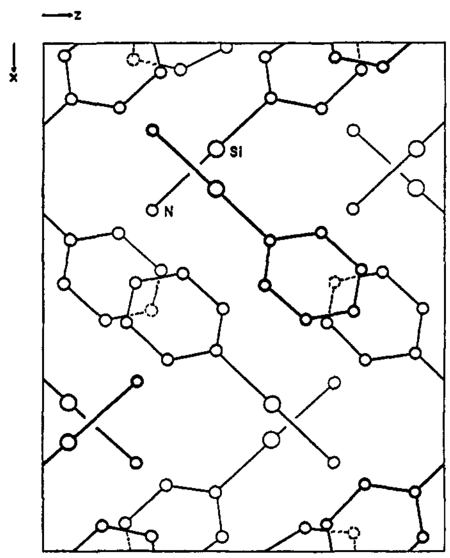

Figure 3. Molecular packing in phenyl-(2,2′,2″-nitrilotriethoxy)-silane with ethoxy bridge atoms omitted for clarity.

the two OCH_2 protons, appear to be magnetically indistinguishable. While crystal disorder invariably introduces some uncertainty into atomic positions, we thought it useful to compare further the two sets of allowed carbon positions. The C′ set determines a plane, $-9.47x - 0.083y + 7.02z = -1.52$, while the C″ set defines the plane $-9.07x - 2.15y + 7.22z = -2.17$. The nitrogen atom is 0.34 Å from the C′ plane and 0.40 Å from the C″ plane on the side toward silicon. The planes are at an angle of 6.7° to each other, at angles of 87.6 and 85.5°, respectively, to the N–Si–C axis, and at angles of 3.3 and 3.8°, respectively, to the plane of the oxygen atoms. Both conformations result in essentially the same distortion of the tetrahedral geometry about nitrogen; the average C–N–Si angles are 103.7 and 105.3° and the average C–N–C angles are 114.6 and 113.1° for the C′ and C″ positions, respectively.

The phenyl group defines a least-squares plane $5.770x + 15.143y + 3.804z = 8.437$ with an average deviation from the plane of 0.008 Å. The angle between the N–Si–C axis and the plane of the phenyl ring is found to be 3.8°, which may represent angular deformation due to lattice packing. In solution, the coplanarity of sp^2 carbon and the atoms bonded to it would certainly be maintained.

The molecular packing is dominated by dipole-dipole interactions ($\mu = 5.98$ D), and no unusually close intermolecular distances were observed. Figure 3 shows the dipole alignment in projection on the (010) plane.

Acknowledgments. We wish to thank C. L. Frye for supplying the compound and for helpful suggestions, and we are grateful to L. C. Shepard and J. J. Flynn for their assistance. Least-squares and Fourier calculations were performed using J. Gvildy's versions of Busing, Martin, and Levy's ORFLS and Shoemaker, Sly, and Van den Hende's ERFR-2, respectively, on the CDC 3800 computer.

Evidence for the Geometric Requirements of Phenyl Migration[1]

William E. Parham and Leonard J. Czuba[1,2]

Contribution from the School of Chemistry of the University of Minnesota, Minneapolis, Minnesota 55455. *Received January 23, 1968*

Abstract: The ring expansion of the hexahydrofluorenone **4** with diazomethane and the related Tiffeneau–Demjanov type of ring expansion of the amino ether **5b** gave products (**6** and **7**) resulting from a ratio of phenyl to cyclohexyl migration of 0.2–0.9:1. This ratio corresponds to a ratio of at least 31:1 for phenyl to alkyl migration in related acyclic systems. These observations are discussed in terms of the geometric requirement for phenyl migration. A new procedure for effecting ring homologation of cyclic ketones by the Tiffeneau–Demjanov ring expansion reaction is described. In this process the desired amino ether **5b** is prepared by hydrocyanation of the corresponding enol ether **15** with subsequent reduction of the derived nitrile **16**. As exemplified by the case under investigation, this modification may be the only suitable method for cases involving unreactive ketones.

The relative migratory aptitudes of a variety of groups have been determined in the rearrangement which accompanies the reaction of acyclic ketones with diazomethane.[3a] From these data it is possible to estimate that the reaction of isopropyl phenyl ketone (**1**) with diazomethane should lead to products resulting from a ratio of phenyl to isopropyl migration of 31:1. Similarly, the deamination of 2-amino-1-isopropyl-1-phenylethanol (**2**) has been reported[3b] to give at least 99% of the product resulting from phenyl migration. The rearrangements in these two reactions (Chart I) are believed to arise from the same intermediate diazonium ion **3**, and the relative migratory aptitudes of various substituents have been shown to be essentially the same in both systems.[3]

Some aspects of steric control of the course of rearrangements involving phenyl migration have been

---

[1] Supported in part by National Science Foundation Grant GP-6169X.

[2] From the Ph.D. Thesis of Leonard J. Czuba, The University of Minnesota, 1967; Sinclair Fellow, 1965–1966.

[3] (a) H. O. House, E. J. Grubbs, and W. F. Gannon, *J. Am. Chem. Soc.*, **82**, 4099 (1960); (b) H. O. House and E. J. Grubbs, *ibid.*, **81**, 4733 (1959).