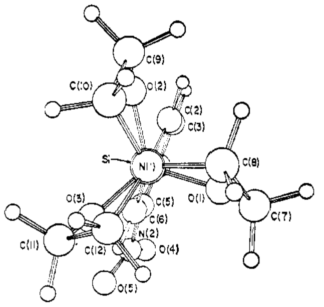

Figure 2. Top view of *m*-nitrophenyl(2,2′,2′′-nitrilotriethoxy)-silane looking down the N–Si–C axis.

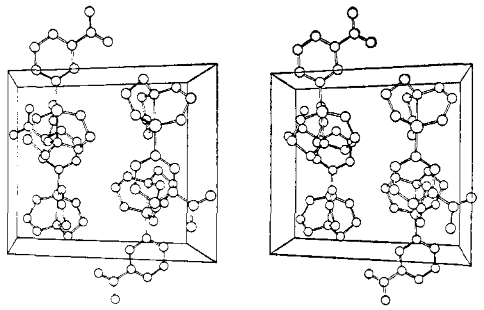

Figure 3. Stereo view of molecular packing in *m*-nitrophenyl(2,2′,-2′′-nitrilotriethoxy)silane.

nitro group is significantly larger than 120°. Other investigators have noted the same effect[15–17] and the suggestion has been made that the strongly electron-withdrawing nitro group causes the C–N bond to have less than one-third s character. The nitro group is twisted by an angle of 16.6° from the plane of the benzene ring, a slightly larger twist angle than is found for *m*-dinitrobenzene (13°)[18] and 3-nitroperchlorylbenzene (13°).[15] Our C–N bond distance of 1.472 Å is shorter than the values found for *m*-dinitrobenzene (1.493 Å),[18] for N-methyl-N,2,4,6-tetranitroaniline (1.490 Å),[19] and for 3-nitroperchlorylbenzene (1.497 Å).[15] It has been observed that this distance is usually shortened in structures with strong resonance interaction between the nitro group and the ring, and the effect of the nitro substituent on the Si–N distance in our structure does require a strong nitro group–phenyl ring interaction.

Molecular packing for this structure is illustrated in Figure 3. Bridge ring 1 is perpendicular to the phenyl ring both internally and externally, but strong dipole–dipole interaction appears to dominate the packing. The shortest intermolecular approach is 3.40 Å.

Acknowledgment. We wish to express our appreciation to Cecil L. Frye who prepared the crystals and to A. H. Case who assisted with the calculations.

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[16] A. S. Bailey and C. K. Prout, *J. Chem. Soc.*, 4867 (1965).

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Structural Studies of Pentacoordinate Silicon. V. Methyl(2,2′,3-nitrilodiethoxypropyl)silane[1]

F. Peter Boer and June W. Turley

Contribution from the Dow Chemical Company, Eastern Research Laboratory, Wayland, Massachusetts 01778, and Chemical Physics Research Laboratory, Midland, Michigan 48640.

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Abstract: The molecular and crystal structure of methyl(2,2′,3-nitrilodiethoxypropyl)silane, $SiO_2NC_8H_{17}$, has been determined by a single-crystal three-dimensional X-ray diffraction study. This compound crystallizes in space group $Pna2_1$, with four molecules per unit cell of dimensions $a = 15.072$, $b = 6.794$, and $c = 9.738$ Å. The intensity data were collected on a Picker automatic diffractometer, and the structure was solved from a Patterson function. All but the methyl hydrogen atoms were located. Full matrix least-squares refinement, including anisotropic thermal parameters for the Si, O, N, and C atoms, gave a final reliability index $R_1 = 0.046$ for 838 reflections. The molecular geometry at silicon is a distorted trigonal bipyramid with the methyl group and the nitrogen atom occupying the apical positions. Bond distances at silicon are Si–N, 2.336; Si–O, 1.663 and 1.669; Si–CH_2–, 1.898; and Si–CH_3, 1.877 (Å). Thus, the silicon atom, at least for the compound in the solid state, is confirmed to be pentacoordinate, although the Si–N bond is relatively long for cage compounds of this type.

Evidence for the presence of pentavalent silicon in cage derivatives of silanes with triethanolamine[2] (I) and 2,2′,2′′-nitrilotriphenol[3] (III) has been obtained in recent X-ray diffraction studies.[4,5] The principal argument for pentavalency was the short Si–N distance, which was interpreted to indicate a transannular Si←:N dative bond, in accord with the large dipole moments observed for these compounds.[6] The Si–N distances were, nevertheless, substantially longer than the sum of the single-bond covalent radii for the two elements, and the possibility that the short distances

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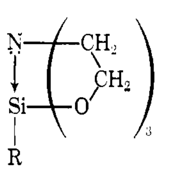
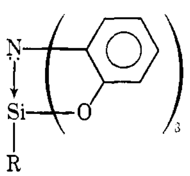


I, R = C_6H_5

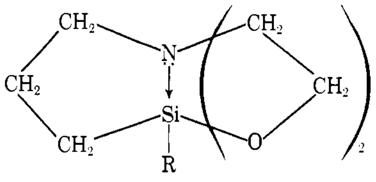
II, R = m-$C_6H_4(NO_2)$



III, R = C_6H_5

arose from steric rather than electronic forces could not finally be ruled out. Therefore, we have carried out additional structure determinations (compound II[1] and this study) to demonstrate that inductive effects in fact give rise to large changes in the Si–N distance that can only be electronic in origin. A number of additional reasons may be adduced for carrying out further work in this area. The crystal structure of compound I was disordered with respect to two alternative nonplanar conformations of the five-membered rings;[4] therefore the ring geometries could not be determined with precision. Also the present study gives substantially improved values for bond distances and angles involving hydrogen.

We report below the molecular and crystal structure of methyl(2,2′,3-nitrilodiethoxypropyl)silane[7] (IV), which may be related formally to I by replacing an oxygen atom by a less electronegative methylene group, and the phenyl ligand by methyl.



IV, R = CH_3

Experimental Section

A long needle-like crystal, of approximate dimensions 0.1 × 0.08 × 4.0 mm, was selected from a sample supplied by Frye, and sealed in a 0.2-mm thin-walled glass capillary tube. A preliminary line-up on the long (c) axis was performed with a Weissenberg camera, and the reciprocal lattice was surveyed for systematic absences. The crystal was then carefully centered on a Picker automatic four-circle diffractometer, and lattice constants were calculated from a least-squares refinement of the setting angles of 10 reflections with Cu Kα radiation (λ 1.5418 Å). The parameters of the orthorhombic cell, $a = 15.072 \pm 0.015$, $b = 6.794 \pm 0.007$, and $c = 9.738 \pm 0.010$ Å, give a calculated density $\rho = 1.246$ g cm^{-3} for $SiO_2NC_8H_{17}$ with $Z = 4$. The systematic absences of $0kl$ reflections for $k + l = 2n + 1$ and $h0l$ for $h = 2n + 1$ are consistent with space groups Pna2_1 or Pnam. A molecular mirror plane perpendicular to the z axis is implied by Pnam, and such a structure appeared unlikely (though not impossible) in view of an expected puckered conformation for the five-membered ring containing the three carbon atoms. Subsequently, the intramolecular vectors in the Patterson map were seen to be inconsistent with this C_s structure, and the final choice of Pna2_1 was made.

The intensity data were collected using the 2θ scan mode of the diffractometer with Ni-filtered Cu Kα radiation. The take-off angle of the tube was 3°, and a counter aperture 4.0 × 4.0 mm was placed 30 cm from the crystal. Scan angles ranging between 2.0 and 2.5° of 2θ were measured at a speed of 2°/min, and two stationary-crystal–stationary-counter background counts of 15 sec were taken at each end of the scan. The reciprocal lattice was recorded out to the instrumental limit ($\sin \theta = 0.9$) and a total of 661 independent reflections[8] was measured. The net intensity, $I = N_0 - kN_b$, for each reflection was assigned an error $\sigma(I) = [(0.05I)^2 + N_0 + k^2N_b]^{1/2}$ where N_0 was the gross count, N_b the background count, and k the ratio of scan time to background time. These σ's were used to calculate the weights $w = 4F^2/\sigma^2(F^2)$ for the least-squares refinement, where the quantity $\Sigma w(|F_0| - |F_c|)^2$ was minimized. Fourteen low-intensity reflections for which $\sigma(I)/I > 0.5$ were regarded as absent and omitted from the refinement, and eight other high-intensity low-order reflections suspected of extinction were eventually dropped from the data set. The intensities were corrected for Lorentz and polarization effects. The linear absorption coefficient is low ($\mu = 17.7$ cm^{-1}) and absorption corrections were not necessary.

Solution and Refinement of Structure[9]

A normal-sharpened three-dimensional Patterson function[9] was analyzed assuming the space group to be Pna2_1. The silicon atoms were located unambiguously at very nearly $^1/_8$, $^1/_4$, 0 and its equivalent sites, where the z coordinate is assigned arbitrarily as permitted by the space group. This conclusion followed, first, from the two largest nonorigin Patterson peaks at $^1/_2$, 0, 0 and $^1/_4$, $^1/_2$, $^1/_2$ (Si–Si interactions); and secondly, from a rough pseudosymmetry, described by the transformations (x, y, z), $(^1/_2 - x, y, z)$, $(^1/_4 + x, ^1/_2 - y, ^1/_2 - z)$, $(^1/_4 - x, ^1/_2 - y, ^1/_2 - z)$, within the true asymmetric unit and arising from the silicon–light atom vectors. In this position, the silicon atoms contributed only to the quarter of the reflection data for which either of the conditions $h = 4n$, $k + l = 2n$ or $h = 4n + 2$, $k + l = 2n + 1$ was satisfied. As might be expected, Fourier synthesis based on silicon alone was not powerful, and gave rise to maps with the same *mmm* ambiguity as the Patterson function.

A chemically reasonable model for the atoms immediately bonded to silicon was inferred from three large Patterson peaks near the origin, which corresponded to O(1), O(2) and a superposition of C(1), C(2), and N. In addition, C(8) gave rise to a well-resolved peak in the vector map and was included in the initial model. Although the other light atoms were not obvious from the Patterson alone, they were inferred by a comparison of the Patterson map with Fourier syntheses based on the "known" atoms. A chemically reasonable model for the whole molecule was thus constructed, but unfortunately we had made the wrong choice with respect to the remaining (x) ambiguity in the orientation of the molecule, and $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ could not be refined below 0.39. The correct model, giving an initial value of $R_1 = 0.31$, was then generated from this false solution by applying the transformation $^1/_4 - x, y, z$.

Five cycles of full-matrix least-squares refinement[10] on the positions and isotropic temperature factors reduced R_1 to 0.087 and $R_2 = \{\Sigma w[F_o - F_c]^2/\Sigma wF_o^2\}^{1/2}$ to 0.141. A Fourier synthesis, from which the electron density of the 12 heavy atoms was subtracted, revealed all the hydrogens (except methyl) with peak heights ranging between 0.15 and 0.50 e/Å^3. The hydrogen atoms were not, however, included in the structure factor calculations at this point. Refinement was continued assuming anisotropic thermal parameters

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[7] E. L. Morehouse, U. S. Patent 3,032,576 (1962); *Chem. Abstr.*, 57, P9981*h* (1962).

[8] The 12.4.5, 0.0.6, 2.0.6, and 4.0.6 reflections were not measured because of instrument malfunction.

[9] Fourier calculations were performed using program B-149 (Argonne National Laboratory), a version of Shoemaker, Sly, and Van den Hende's ERFR-2, by J. Gvildys.

[10] (a) Least-squares and structure factor calculations were performed using ANL-FLS-14E, J. Gvildys's version of Busing, Martin, and Levy's OR-FLS. (b) Atomic scattering factors were taken from "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 201.

Table I. Final Structure Parameters[a] and Standard Errors[b]

Atom	x/a	y/b	z/c	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Si	0.1228 (1)	0.2497 (1)	0.0000	26 (1)	139 (2)	72 (1)	−1 (1)	5 (1)	−4 (1)
O(1)	0.1188 (2)	0.4909 (4)	−0.0281 (4)	52 (1)	154 (5)	78 (4)	−2 (4)	9 (1)	16 (3)
O(2)	0.0280 (1)	0.1254 (3)	−0.0180 (4)	30 (1)	202 (4)	87 (3)	−15 (2)	7 (2)	−31 (3)
N	0.0498 (2)	0.3490 (4)	0.1999 (5)	33 (1)	171 (6)	69 (3)	−1 (2)	−17 (2)	−5 (4)
C(1)	0.1760 (3)	0.1744 (7)	−0.1662 (6)	40 (2)	253 (10)	121 (6)	−3 (3)	26 (3)	−24 (6)
C(2)	0.2054 (3)	0.1625 (7)	0.1339 (6)	31 (1)	254 (10)	126 (6)	10 (3)	−7 (2)	16 (6)
C(3)	0.1693 (3)	0.1381 (7)	0.2778 (6)	45 (2)	270 (11)	102 (6)	15 (3)	−11 (3)	34 (6)
C(4)	0.1120 (3)	0.3142 (8)	0.3156 (6)	49 (2)	253 (10)	68 (5)	−8 (4)	−10 (2)	3 (6)
C(5)	0.1032 (3)	0.6312 (5)	0.0788 (6)	63 (2)	137 (7)	107 (6)	−1 (3)	0 (3)	−10 (5)
C(6)	0.0307 (2)	0.5555 (5)	0.1709 (6)	52 (2)	182 (8)	95 (5)	19 (3)	−4 (2)	−18 (5)
C(7)	−0.0505 (2)	0.1693 (6)	0.0575 (6)	29 (1)	265 (9)	98 (5)	−13 (3)	5 (2)	−8 (6)
C(8)	−0.0286 (2)	0.2196 (6)	0.2028 (6)	34 (2)	254 (8)	84 (5)	−13 (3)	12 (2)	0 (6)

Hydrogens

Atom	x/a	y/b	z/c	B
H(2A)	0.230 (2)	0.037 (6)	0.095 (5)	3.3 (0.8)
H(2B)	0.246 (4)	0.245 (7)	0.142 (7)	4.8 (1.3)
H(3A)	0.149 (4)	0.003 (10)	0.284 (7)	5.9 (1.2)
H(3B)	0.210 (5)	0.167 (11)	0.355 (10)	8.5 (2.0)
H(4A)	0.154 (3)	0.432 (7)	0.334 (6)	4.5 (1.0)
H(4B)	0.063 (4)	0.284 (8)	0.389 (8)	5.9 (1.3)
H(5A)	0.086 (4)	0.749 (8)	0.033 (6)	4.5 (1.0)
H(5B)	0.171 (5)	0.662 (8)	0.122 (10)	5.9 (1.3)
H(6A)	0.016 (4)	0.622 (8)	0.259 (10)	4.5 (1.0)
H(6B)	−0.035 (2)	0.560 (5)	0.141 (5)	8.8 (1.8)
H(7A)	−0.083 (4)	0.269 (9)	0.009 (7)	6.4 (1.3)
H(7B)	−0.096 (3)	0.052 (8)	0.070 (6)	2.8 (0.7)
H(8A)	−0.020 (4)	0.101 (8)	0.265 (9)	5.3 (1.1)
H(8B)	−0.081 (3)	0.274 (5)	0.258 (4)	5.5 (1.1)

[a] The anisotropic thermal parameters are in the form $\exp(-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}))$. [b] Standard errors are given in parentheses.

for the heavy atoms; after two cycles R_1 was reduced to 0.065 and R_2 to 0.101. A second difference map again revealed the fourteen nonmethyl hydrogen atoms. The peak heights now ranged between 0.19 and 0.35 e/Å^3 and in general the peaks were more clearly resolved and the bond distances were more reasonable than in the earlier map. Refinement was completed in five additional cycles of least squares in which all positional parameters, heavy atom anisotropic thermal parameters, and hydrogen isotropic thermal parameters were simultaneously varied.[11] The final discrepancy indices were $R_1 = 0.046$ and $R_2 = 0.059$. During the course of the refinement eight high-intensity low-order reflections (020, 011, 200, 210, 201, 002, 203, and 400) suspected of extinction were removed from the data set. A final difference map revealed some peaks as high as 0.50 e/Å^3 near the silicon atom and additional electron density (0.22 e/Å^3) in the region occupied by the methyl hydrogens, which appeared to be disordered.

Atomic parameters and their estimated standard deviations are given in Table I, while bond distances and angles, together with standard deviations computed[12] from the variance–covariance matrix obtained from the final least-squares cycle, are listed in Table II. The root-mean-square components of thermal displacement along the principal axes, as defined by the anisotropic thermal parameters, are compiled in Table III. The directions of thermal motion may be inferred from Figure 1, in which the three-dimensional structure of the molecule is shown using ellipsoids to represent the anisotropic thermal motion.[13] A table of observed and calculated structure factors is available to the interested reader.[14]

Results and Discussion

Methyl(2,2′,3-nitrilodiethoxypropyl)silane (IV) has the distorted trigonal-bipyramidal geometry observed[1,4,5] for I, II, and III. These four compounds show some interesting variations in structural parameters as substitutents at nitrogen and at both the equatorial and axial sites of silicon are changed. A comparison of the Si–N and Si–C bond lengths (Table IV) is especially revealing. Taking the phenylnitrilotriethoxysilane[4] (I) as a standard, we find that the Si–N bond distance shortens from 2.193 to 2.116 Å upon replacement[1] of the axial phenyl ligand by the more powerfully electron-withdrawing *m*-nitrophenyl group (II). Because force constants in the rings are not changed by this substitution, this reduction in distance must be purely electronic in origin: as charge is withdrawn from silicon, its ability to accept lone-pair electrons from nitrogen is enhanced. In the present structure IV, the replacement of one of the three equatorial oxygen ligands by a less electronegative methylene group produces an effect in the opposite direction: the ability of silicon to accept electrons is now reduced and the observed Si–N distance of 2.336 Å

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(11) Hydrogen scattering factors are by R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(12) J. Gvildy's version (ANL Program Library B-115) of Busing, Martin, and Levy's Fortran function and error program, OR-FFE, was used.

(13) ORTEP is a Fortran thermal ellipsoid plot program by C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(14) Material supplementary to this article has been deposited as Document No. NAPS-00317 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, N. Y. 10001. A copy may be secured by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Table II. Distances and Angles[a]

A. Bond Distances (Å)

Si-O(1)	1.663 (3)	C(2)-H(2A)	1.00 (4)
Si-O(2)	1.669 (2)	C(2)-H(2B)	0.84 (5)
Si-N	2.336 (4)	C(3)-H(3A)	0.97 (7)
Si-C(1)	1.877 (5)	C(3)-H(3B)	0.99 (10)
Si-C(2)	1.898 (5)	C(4)-H(4A)	1.04 (5)
O(1)-C(5)	1.431 (5)	C(4)-H(4B)	1.05 (7)
O(2)-C(7)	1.425 (4)	C(5)-H(5A)	0.95 (6)
N-C(4)	1.486 (5)	C(5)-H(5B)	1.12 (8)
N-C(6)	1.459 (4)	C(6)-H(6A)	0.99 (9)
N-C(8)	1.472 (5)	C(6)-H(6B)	1.03 (3)
C(2)-C(3)	1.513 (7)	C(7)-H(7A)	0.96 (6)
C(3)-C(4)	1.520 (7)	C(7)-H(7B)	1.06 (5)
C(5)-C(6)	1.505 (6)	C(8)-H(8A)	1.01 (7)
C(7)-C(8)	1.492 (7)	C(8)-H(8B)	1.02 (4)

B. Bond Angles (degrees)

Vertex	Atom 1	Atom 2		Vertex	Atom 1	Atom 2	
Si	O(1)	O(2)	116.7 (0.1)	O(1)	Si	C(5)	122.9 (0.3)
	O(1)	N	80.5 (0.1)	O(2)	Si	C(7)	123.4 (0.2)
	O(1)	C(1)	98.2 (0.2)	N	Si	C(4)	106.8 (0.3)
	O(1)	C(2)	116.4 (0.2)		Si	C(6)	102.1 (0.3)
	O(2)	N	80.2 (0.1)		Si	C(8)	102.8 (0.3)
	O(2)	C(1)	97.9 (0.1)		C(4)	C(6)	115.1 (0.3)
	O(2)	C(2)	118.4 (0.2)		C(4)	C(8)	113.4 (0.3)
	N	C(1)	176.8 (0.2)		C(6)	C(8)	114.8 (0.3)
	N	C(2)	80.0 (0.2)				
	C(1)	C(2)	103.1 (0.2)				
C(2)	Si	C(3)	115.7 (0.3)	C(6)	N	C(5)	107.5 (0.3)
	Si	H(2A)	104 (2)		N	H(6A)	108 (4)
	Si	H(2B)	110 (4)		N	H(6B)	106 (2)
	C(3)	H(2A)	113 (3)		C(5)	H(6A)	122 (3)
	C(3)	H(2B)	104 (4)		C(5)	H(6B)	121 (2)
	H(2A)	H(2B)	110 (4)		H(6A)	H(6B)	91 (4)
C(3)	C(2)	C(4)	110.0 (0.4)	C(7)	O(2)	C(8)	110.7 (0.3)
	C(2)	H(3A)	106 (4)		O(2)	H(7A)	109 (4)
	C(2)	H(3B)	117 (5)		O(2)	H(7B)	116 (3)
	C(4)	H(3A)	123 (3)		C(8)	H(7A)	115 (4)
	C(4)	H(3B)	90 (4)		C(8)	H(7B)	102 (3)
	H(3A)	H(3B)	110 (6)		H(7A)	H(7B)	105 (5)
C(4)	N	C(3)	107.4 (0.4)	C(8)	N	C(7)	107.2 (0.3)
	N	H(4A)	113 (3)		N	H(8A)	113 (3)
	N	H(4B)	96 (4)		N	H(8B)	114 (2)
	C(3)	H(4A)	107 (3)		C(7)	H(8A)	114 (4)
	C(3)	H(4B)	114 (3)		C(7)	H(8B)	114 (2)
	H(4A)	H(4B)	118 (5)		H(8A)	H(8B)	94 (5)
C(5)	O(1)	C(6)	109.0 (0.3)				
	O(1)	H(5A)	105 (4)				
	O(1)	H(5B)	105 (4)				
	C(6)	H(5A)	112 (3)				
	C(6)	H(5B)	120 (5)				
	H(5A)	H(5B)	106 (4)				

[a] Standard errors calculated from the variance–covariance matrix obtained in the final least-squares cycle are given in parentheses.

is much longer than the values in I and II. (In this case, the substitution of a methyl group for the axial phenyl ligand may also play a small role in weakening the Si–N bond, and the change in a force constant in one of the three five-membered rings may also have a minor effect.) A weakening of the Si–N bond can also result when the basicity of the nitrogen atom is reduced inductively by substituents. This circumstance arises in phenylnitrilotriphenoxysilane[5] (III), where the bridging ethoxy groups of I have been replaced by their phenoxy analogs. The Si–N interaction of 2.344 Å is again relatively long; we note, however, that the replacement of sp^3- by sp^2-hybridized carbons in the five-membered rings must also affect this distance.

Thus, these four structure determinations demonstrate that inductive forces can cause the Si–N distances in these cage compounds to vary over a range of at least 0.23 Å, and that all of the changes are readily explained in terms of a Si←:N dative bond. In fact, the axial Si–C bond directly opposite the Si–N interaction also shows an interesting variability. When their distances are corrected for change in bond radius due to carbon hybridization (to a common sp^2 basis), the Si–C bonds are readily seen (Table IV) to become uniformly weaker as

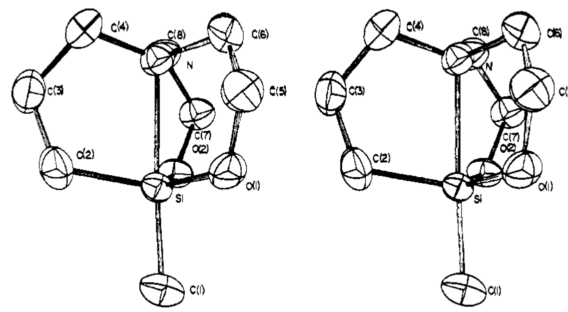

Figure 1. Three-dimensional view of the molecular structure of methyl(2,2′,3-nitrilodiethoxypropyl)silane, showing ellipsoids of thermal motion.

the Si–N bonds become stronger, and their bond lengths range from 0.01 to 0.06 Å longer than the Si–C distance in a tetravalent standard, phenylsilane.[15] This rather small effect also militates toward a pentavalent model.

Table III. Root-Mean-Square Thermal Displacements along Principal Axes[a,b] (Å)

Atom	Axis 1	Axis 2	Axis 3
Si	0.167 (2)	0.179 (2)	0.193 (2)
O(1)	0.174 (4)	0.204 (4)	0.248 (3)
O(2)	0.177 (3)	0.184 (4)	0.243 (3)
N	0.181 (5)	0.196 (4)	0.201 (4)
C(1)	0.178 (5)	0.238 (5)	0.275 (6)
C(2)	0.181 (5)	0.236 (5)	0.254 (5)
C(3)	0.188 (5)	0.243 (5)	0.264 (5)
C(4)	0.175 (6)	0.233 (5)	0.251 (5)
C(5)	0.177 (5)	0.228 (6)	0.269 (4)
C(6)	0.190 (5)	0.215 (5)	0.256 (4)
C(7)	0.176 (4)	0.217 (5)	0.253 (4)
C(8)	0.174 (5)	0.217 (5)	0.249 (4)
H(2A)	0.204		
H(2B)	0.247		
H(3A)	0.272		
H(3B)	0.328		
H(4A)	0.239		
H(4B)	0.274		
H(5A)	0.237		
H(5B)	0.334		
H(6A)	0.284		
H(6B)	0.189		
H(7A)	0.258		
H(7B)	0.264		
H(8A)	0.294		
H(8B)	0.165		

[a] Ordered on increasing magnitude. [b] Standard errors, multiplied by 10^3, are given in parentheses as computed from the variance–covariance matrix obtained in the final least-squares cycle.

The coordination at silicon in IV (Figure 1) is distorted from an ideal trigonal-bipyramid geometry by a bending of the three equatorial substituents toward the nitrogen. The angles N–Si–O(1), 80.5°; N–Si–O(2), 80.2°; and N–Si–C(2), 80.0°, are each about 10° less than the 90° value for an ideal trigonal bipyramid and are nearly the same as the angles observed[5] for compound III. Perhaps because of the asymmetry of the three equatorial ligands, the Si–N and Si–C bonds are not quite collinear, forming an angle of 176.8°. This small distortion increases the C(1)–Si–C(2) angle to 103.1° and reduces the two C(1)–Si–O angles to 98.2 and 97.9°. The silicon–oxygen bond lengths, 1.663 and 1.669 Å, are about what might be expected in compounds of this kind. The fact that the equatorial Si–C bond (1.898 ± 0.005 Å) is observed to be slightly longer than the axial bond (1.877 ± 0.005 Å) contravenes the usual rule for trigonal bipyramids;[16] we hesitate however to attach too much experimental or theoretical significance to this observation.

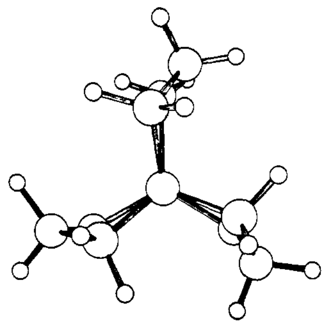

Figure 2. A view of methyl(2,2′,3-nitrilodiethoxypropyl)silane looking down the N–Si–CH_3 axis. Hydrogen atoms are shown.

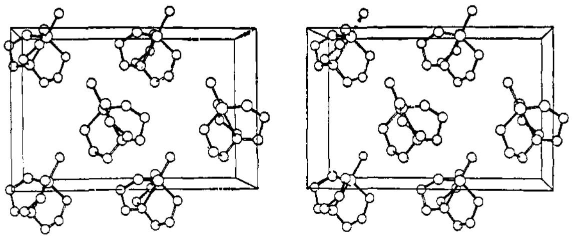

Figure 3. Three-dimensional diagram of the molecular packing in a unit cell of methyl(2,2′,3-nitrilodiethoxypropyl)silane. The origin is at the rear in the upper left corner, the x axis is horizontal, the z axis is vertical, and the y axis points toward the viewer.

The geometry at nitrogen is concave, but again we find an asymmetry in the three bridges, with the carbon atom from the propyl chain forming a larger angle (106.8°) with the Si–N axis than the two carbons of the ethoxy chains (102.1 and 102.8°). The bond angles at carbon are all fairly close to the tetrahedral value of 109.5°, with the exception of the angle Si–C(2)–C(3), which is opened up to 115.7°, bringing it nearer to the structurally analogous Si–O–C angles (122.9 and 123.4°). The C–C, C–N, and C–O bond distances appear to be normal. The 14 C–H distances average 1.00 Å with an rms deviation of 0.065 Å for the group. This average is as expected shorter than the accepted value for a C(sp^3)–H bond of 1.09 Å, and results from a bias of the electron density at hydrogen away from the nucleus and toward the bond region.

The geometries of the five-membered rings, including the hydrogen atoms, can be seen most clearly in Figure 2. The three rings are in very similar envelope conformations, each folded in the same sense with respect to a rotation about the Si–N axis. Interestingly, the atoms β to the nitrogen, namely C(3), C(5), and C(7), are the ones bent out of plane; in compounds I and II, where the Si–N bond was substantially shorter, the three α carbons were out of plane.[1,4] The equatorial bonds of the silicon atom eclipse the N–C bonds fairly closely: the angle between Si–C(2) and N–C(4) is 7.3 ± 0.3°, while the pairs Si–O(1), N–C(6), and Si–O(2), N–C(8) form angles of 9.2 and 9.0 ± 0.2°,

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

(16) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).

Table IV. Comparison of Pentavalent Silicon Geometries

Compd	d(Si-N)	d(Si-C)	Av d(Si-O)	Av $\angle$C-Si-O, deg	Ref
II	2.116 (6)	1.905 (7)	1.656	95.8	1
I	2.193 (5)	1.882 (6)	1.656	97.1	4
IV	2.336 (4)	1.857 (5)[a]	1.666	98.1	This work
III	2.344 (5)	1.853 (6)	1.642	100.0	5
Phenylsilane		1.843 (5)			15

[a] All of the compounds are sp^2 hybridized except IV. The Si-C carbon distance in IV has been corrected by 0.020 A from the observed value of 1.877 Å to take into account the difference between sp^3 and sp^2 covalent radii [L. N. Ferguson "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963, p 39].

respectively. The puckering in the rings can be measured in terms of certain dihedral angles formed between planes each defined by three atoms; for example, {Si-N-C(2), C(2)-C(3)-C(4)}, 140.4 ± 0.5°; {Si-N-O(1), O(1)-C(5)-C(6)}, 144.6 ± 0.4°; and {Si-N-O(2), O(2)-C(7)-C(8)}, 146.8 ± 0.4°.

The molecular packing, shown in Figure 3, is dominated by dipole-dipole interactions, and no unusually short intermolecular contacts occur. A characteristic mode of packing[4,5] in these compounds is for one of the bridging groups to tuck in the angle between two bridging groups on an adjacent molecule. In methyl(2,2′,3-nitrilodiethoxypropyl)silane, the bridge O(1)-C(5)-C(6) nests between the bridges C(2)-C(3)-C(4) and O(2)-C(7)-C(8) of the molecule related by a cell translation along y.

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Heptafulvalene Cation and Anion Radicals

M. D. Sevilla, S. H. Flajser, G. Vincow,[1] and H. J. Dauben, Jr.[2]

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. *Received October 16, 1968*

Abstract: The cation and anion radicals of heptafulvalene (I) have been prepared and their esr spectra have been investigated. This study has been conducted in order to gain information concerning resonance stabilization and spin-density distributions in molecules closely related to the nonbenzenoid hydrocarbon heptafulvalene. The heptafulvalene cation (III) is generated by thermal cleavage of the dication dimer ($30° \lesssim t \lesssim 60°$) and the anion is produced by reaction of potassium with I at *ca.* $-80°$ and by cleavage of the dianion dimer at temperatures greater than 30°. The hyperfine spectrum of the cation radical is consistent with three sets of four protons each with splittings $|a_1^H| = 0.075$ G, $|a_2^H| = 2.90$ G, and $|a_3^H| = 1.72$ G. The anion-radical spectrum is very temperature and solvent dependent due to intramolecular potassium ion migration. Both slow-exchange and rapid-exchange spectra are observed. The slow-exchange spectrum ($-120°$; MTHF) arises from two groups of two protons each with splittings $|a_1^H| = 8.22$ G and $|a_3^H| = 5.02$ G. Comparison of these couplings with those of the rapid-exchange spectra and with calculated splittings reveals a feature of the spin-density distribution which is novel—the unpaired spin in heptafulvalene anion is essentially localized on one of the rings. Two pieces of evidence provide indications that the radical ions of heptafulvalene, in contrast with heptafulvalene itself, may have considerable delocalization energy as predicted by HMO theory: (1) the dimers of the radical ions are appreciably dissociated at room temperature, and (2) good agreement is obtained between the experimental hyperfine splittings and the values computed using approximate π-electron theory in which a uniform nuclear framework is assumed, thus indicating an absence of the alternating single and double bonds which reduce the delocalization energy of I.

The resonance stabilization of nonbenzenoid hydrocarbons is of considerable interest. Heptafulvalene (I) is predicted by HMO theory to possess a large delocalization energy in disagreement with the experimental finding of a small empirical resonance energy.[3] It would be of interest to gain information regarding resonance stabilization for molecules with the same nuclear framework as I which are related to it by π-electron oxidation and reduction.[4] Toward this end we have prepared the heptafulvalene cation and anion radicals and have investigated their esr spectra.

This study also comprises a continuation of our investigations of spin density distributions for π-electron hydrocarbon radicals containing seven-membered rings.[5]

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(1) (a) Alfred P. Sloan Research Fellow; (b) to whom all inquiries should be addressed.

(2) Deceased April 3, 1968.

(3) R. B. Turner, "Theoretical Organic Chemistry; Kekulé Symposium," Butterworth & Co. (Publishers), Ltd., London, 1959, p 67.

(4) As far as we are aware only one such molecule has been prepared to date, the heptafulvalene dication [I. S. Akhrem, E. I. Fedin, B. A. Kvasov, and M. E. Vol'pin, *Tetrahedron Letters*, 5265 (1967)].

(5) (a) G. Vincow, M. L. Morrell, W. V. Volland, H. J. Dauben, Jr., and F. R. Hunter, *J. Am. Chem. Soc.*, **87**, 3527 (1965); (b) G. Vincow, M. L. Morrell, F. R. Hunter, and H. J. Dauben, Jr., *J. Chem. Phys.*, **48**, 2876 (1968); (c) W. V. Volland and G. Vincow, *ibid.*, **48**, 5589 (1968).

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