Organic and Biological Chemistry

Structural Studies of Pentacoordinate Silicon. IV. *m*-Nitrophenyl(2,2′,2″-nitrilotriethoxy)silane[1]

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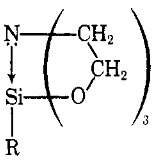
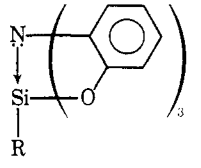
Abstract: The molecular and crystal structures of *m*-nitrophenyl(2,2′,2″-nitrilotriethoxy)silane, $SiO_5N_2C_{12}H_{16}$, have been determined by three-dimensional X-ray diffraction methods. This material crystallizes in space group $P2_1/c$ with $a = 10.102$, $b = 11.013$, and $c = 12.961$ Å, $\beta = 110.28°$, and $Z = 4$. The intensity data were collected on a Picker automatic diffractometer and the structure was solved by direct methods. All hydrogen atoms were located. Refinement by full-matrix least-squares gave a final reliability index of $R_1 = 0.061$ for 1350 reflections above background. The molecular geometry at silicon is a distorted trigonal bipyramid, but the distortion, as measured by the average C–Si–O angle of 95.8°, is less than that found for the other structures in this series. Also, the Si–N distance of 2.116 Å is shorter than observed previously. The three equatorial Si–O distances are 1.656, 1.661, and 1.650 Å, and the Si–C distance is 1.904 Å. The plane of the nitro group is at an angle of 16.6° to the plane of the phenyl ring, and the N–O distances are 1.239 and 1.203 Å.

The determination of the structures of phenyl(2,2′,2″-nitrilotriethoxy)silane (I)[2] and phenyl(2,2′,2″-nitrilotriphenoxy)silane (II)[3] has indicated the presence of pentavalent silicon in these compounds *via* transannular dative bonds between silicon and nitrogen. The coordination at silicon in these structures was of a distorted trigonal bipyramidal type, while the geometry at nitrogen was observed to be concave. Further studies of this system have been undertaken to demonstrate that these structural features are electronic rather than steric in origin. In this paper we report the structure of a nitro derivative of I, *m*-nitrophenyl(2,2′,2″-nitrilotriethoxy)silane (III). This study also provides a more detailed description of the bridging atoms in these caged compounds; the geometry in compound I was obscured to some degree by disorder in the positions of the three carbon atoms bonded directly to nitrogen. We shall, however, defer a more comprehensive discussion of the comparative features of these structures to the following paper.[4]



I, $R = C_6H_5$

III, $R = m\text{-}C_6H_4(NO_2)$



II, $R = C_6H_5$

Experimental Section

Data Collection. *m*-Nitrophenyl(2,2′,2″-nitrilotriethoxy)silane is prepared by conventional techniques using triethanolamine and nitrophenyltriethoxysilane,[5] and forms colorless flat prisms with well-developed faces. The space group, $P2_1/c$, was determined by the Weissenberg technique from the observed reflection conditions $h0l$, $l = 2n$; and $0k0$, $k = 2n$ and the reciprocal lattice symmetry of C_{2h}. 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.[6] Reference lines were provided by a 7.5-μ Al foil used as the sample holder. The unit cell dimensions obtained from the Weissenberg data were refined by the method of axial ratios[7] using the powder data to give $a = 10.102 \pm 0.005$, $b = 11.013 \pm 0.013$, and $c = 12.961 \pm 0.012$ Å, and $\beta = 110.28 \pm 0.50°$ for the monoclinic cell. The calculated density of 1.454 g/cc corresponds to four molecules per cell.

A crystal of approximate dimensions 0.2 × 0.4 × 0.1 mm was mounted on the long (b) axis and carefully centered on the goniometer of a Picker automatic diffractometer. Intensity data were collected using the 2θ scan mode of the diffractometer with Cu Kα radiation (λ 1.5418 Å) selected by a monochromator using the 1,0,0 reflection of a highly oriented graphite crystal.[8] Settings were based on a reference set of nine reflections measured manually. The take-off angle for the X-ray tube was 3°, and a scintillation detector with a 4.0-mm square aperture was placed 26 cm from the crystal. Variable-scan angles from 1.9 to 2.5° were used with a scan speed of 1°/min over the range (0–133°) of 2θ investigated. Background counts of 10 sec were taken at each end of the scan using the stationary-crystal–stationary-counter technique. An error $\sigma(I) = [(0.03I)^2 + N_0 + k^2N_b]^{1/2}$ was assigned to the net intensities, $I = N_0 - kN_b$, and used to calculate the weights $w = 4F^2/\sigma^2(F^2)$ for the least-squares structure refinement minimizing $\Sigma w(F_o - F_c)^2$. Here N_0 is the gross count, N_b is the background count, and k is the ratio of scan time to background time. The data were next corrected for Lorentz and polarization effects using the expression $Lp^{-1} = (2 \sin 2\theta)/(\cos^2 2\theta_m + \cos^2 2\theta)$ corresponding to the Picker geometry with a crystal monochromator setting of θ_m.

A total of 2661 unique reflections were measured. These included 142 systematically absent reflections. When the criterion, $\sigma(I)/I \leq 0.3$, was used to distinquish observed from nonobserved reflections, 25 of the extinct reflections appeared to be observed. When the criterion was reset to $\sigma(I)/I \leq 0.2$, the extinct reflections were correctly grouped, and a set of 1440 reflections "above back-

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(1) Paper III: F. P. Boer, J. J. Flynn, and J. W. Turley, *J. Am. Chem. Soc.*, 90, 6973 (1968).

(2) J. W. Turley and F. P. Boer, *ibid.*, 90, 4026 (1968).

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(5) C. L. Frye, G. E. Vogel, and T. A. Hall, *ibid.*, **83**, 996 (1961).

(6) E. Hoffman and H. Jagodzinski, *Z. Metallk.*, **46**, 601 (1955).

(7) L. K. Frevel, *Acta Cryst.*, 17, 907 (1964).

(8) T. C. Furnas, Jr., and D. W. Beard, Abstract E3, Summer Meeting, American Crystallographic Association, University of Minnesota, Minneapolis, Minn., Aug 20–25, 1967.

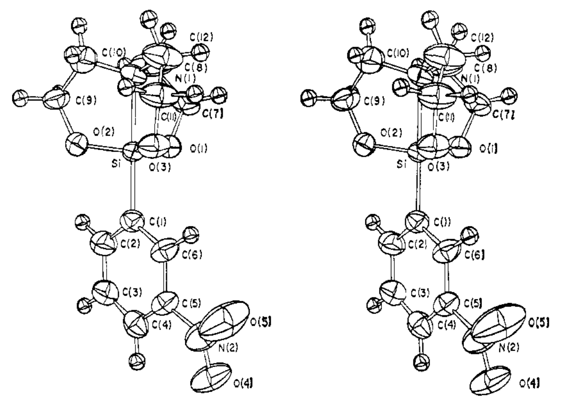

Figure 1. Stereo view of *m*-nitrophenyl(2,2′,2″-nitrilotriethoxy)-silane with atoms drawn as 50% probability ellipsoids of thermal motion.

ground" was obtained. Absorption corrections have not been applied to the data; errors from this effect should not be serious in view of the low linear absorption coefficient $\mu(\text{Cu K}\alpha) = 17.2\ \text{cm}^{-1}$ and the relatively small crystal size. An absolute scale factor and over-all temperature factor were calculated from the data by Wilson's method.

Structure Determination. Iterative application of Sayre's equation[9] in three dimensions led immediately to the solution of the structure. The equation is

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

where s means "sign of," *a*, *b*, and *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. A set of 339 reflections having $|E| \geq 1.5$ and a starting set comprising three origin-determining reflections ($\bar{3}$.1.2, $\bar{7}$.2.14, 2.6.5) assigned positive phases and four additional reflections (1.1.8, 1.1.6, $\bar{1}$.5.1, $\overline{12}$.1.6) with both positive and negative phases allowed were used with an automated computer program.[10a] Iteration on the 16 starting phase sets gave a consistency index

$$C = \frac{\left\langle \left| E_a \sum_{a=b+c} E_bE_c \right| \right\rangle}{\left\langle |E_a| \sum_{a=b+c} |E_b||E_c| \right\rangle} = 0.865$$

for the $[-++-]$ starting set after 8 cycles. No other trial set converged in fewer than 15 cycles; the values of *C* ranged between 0.391 and 0.687 for these other solutions. An *E* map[10b] based on the $[-++-]$ solution gave the expected chemical structure except for the atoms of the nitro group which appeared as unusually low peaks. The final refinement showed fairly high thermal parameters for these three atoms in agreement with the *E* map result.

Structure Refinement. Initial atomic positions read from the *E* map were refined by full-matrix least-squares[10c,11] for three cycles holding the over-all temperature factor *B* constant at a value of 3.0 for all atoms. Reliability indices at this point were $R_1 = \Sigma|F_o - F_c|/\Sigma|F_o| = 0.197$ and $R_2 = \{\Sigma w(F_o - F_c)^2/\Sigma wF_o^2\}^{1/2} = 0.233$. Next, three cycles of isotropic refinement giving $R_1 = 0.125$ and $R = 0.163$ were followed by four cycles of anisotropic refinement dropping R_1 to 0.090 and $R_2 = 0.111$. A careful study of the data set after these calculations showed a subset of 90 very weak reflections for which $\Delta F/F_o \geq 2.0$, and these reflections were omitted from subsequent refinements. An additional three cycles of anisotropic refinement after this adjustment gave $R_1 = 0.076$ and $R_2 = 0.091$. Positions for the 16 hydrogen atoms in the structure were calculated using a computer program which assumes ideal sp^3 and sp^2 bonding for carbon, and all hydrogens were also found in essentially the calculated positions on a difference map based on the most recent anisotropic refinement. Three cycles of isotropic refinement on the hydrogens holding all other atoms constant gave $R_1 = 0.0648$ and $R_2 = 0.0744$. The errors in the hydrogen parameters were found to be quite large. Following this, three cycles of anisotropic refinement on C, N, O, and Si holding the hydrogens constant gave the final reliability indices $R_1 = 0.0607$ and $R_2 = 0.0697$. The average *x*, *y*, and *z* parameter shift in the final cycle was 0.01σ with a maximum shift of 0.04σ. Final atomic parameters and their estimated standard deviations are given in Table I, and bond distances and angles are listed in Table II.[10d] A table of observed and calculated structure factors from the final cycle of least-squares refinement has been deposited with the ASIS National Auxiliary Publication Service as Document No. NAPS-00316.[12]

Results and Discussion

The molecular structure is shown in Figure 1.[10e] As in structures I and II, the geometry at silicon is a distorted trigonal bipyramid with the oxygen atoms bent away from the phenyl group and toward the nitrogen. The nitro derivative shows less distortion of the silicon bonding geometry than do the other structures. The average C-Si-O angle is 95.8°, somewhat closer to the 90° angle of an ideal trigonal bipyramid than the 100.0° value found in II or the 97.1° value in I. This molecule also has the shortest Si-N bond distance (2.116 Å) observed in this series; the substantial reduction in distance from the value of 2.193 Å in compound I is directly attributable to the inductive effect of the strongly electron-withdrawing nitro group. The Si-C bond distance of 1.904 Å is 0.061 Å greater than the bond distance in phenylsilane,[13] and follows the usual rule that axial bonds in trigonal bipyramids are apt to be lengthened[14] (see also ref 4). The N-Si-C axial atoms are collinear with an average deviation of 0.008 Å from their least-squares line[10f] (described by the parametric equations $\{x = 0.2680 + 0.0370t;\ y = 0.2085 + 0.0845t;\ z = 0.2471 + 0.0020t\}$). Seven planes in the structure were fit by least-squares[10f] and their equations are given in Table III. Dihedral angles of interest are given in Table IV. The angles between the Si-C-N line and (1) the plane of the phenyl ring, (2) the carbons bonded to nitrogen, and (3) the oxygens show that the amount of distortion from ideal trigonal-bipyramid geometry in this structure is fairly small and occurs mainly as a displacement of the plane of the oxygen atoms to-

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(9) D. Sayre, *Acta Cryst.*, **5**, 60 (1952).

(10) Computers and programs used are as follows: (a) 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 (CDC 3800); (b) J. Gvildys, "Two- and Three-Dimensional Crystallographic Fourier Summation Program," based on MIFRI, Program Library B-149, Argonne National Laboratory, Applied Mathematics Division, Argonne, Ill., April 13, 1965 (CDC 3800); (c) J. Gvildys, "A Fortran Crystallographic Least-Squares Refinement Program," based on OR-FLS, Program Library 14E7043, Argonne National Laboratory, Applied Mathematics Division, Argonne, Ill., March 31, 1967 (CDC 3800); (d) J. Gvildys, "ANL-FFE, A Fortran Crystallographic Function and Error Program," based on OR-FFE, Program Library B 115, Argonne National Laboratory, Applied Mathematics Division, Argonne, Ill., Sept 17, 1964 (CDC 3800); (e) C. K. Johnson, "OR-TEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., June 1965 (IBM 7094); (f) J. Gvildys, "Least-Squares Plane and Line Fitter," see V. Shomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, **12**, 600 (1959), Program Library B-125, Argonne National Laboratory, Applied Mathematics Division, Argonne, Ill., May 18, 1965 (CDC 3800).

(11) Atomic scattering factors were taken from "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–209. Hydrogen scattering factors are by R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

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(14) R. J. Gillespie, *J. Chem. Soc.*, 4673 (1963).

Table I. Final Atomic Parameters

Atom	Atomic coordinates[a] x	y	z	B
C(1)	0.19516 (53)	0.04151 (51)	0.24277 (46)	
C(2)	0.12250 (69)	−0.01457 (61)	0.14242 (53)	
C(3)	0.07950 (66)	−0.13674 (63)	0.13657 (58)	
C(4)	0.10795 (60)	−0.20825 (61)	0.22828 (54)	
C(5)	0.18161 (59)	−0.15326 (53)	0.32519 (52)	
C(6)	0.22602 (62)	−0.02936 (55)	0.33602 (51)	
C(7)	0.51703 (66)	0.24846 (67)	0.22670 (63)	
C(8)	0.44934 (85)	0.37361 (70)	0.19754 (80)	
C(9)	0.12850 (66)	0.37265 (59)	0.09656 (51)	
C(10)	0.21964 (84)	0.45454 (69)	0.18577 (68)	
C(11)	0.30875 (78)	0.35190 (63)	0.42262 (54)	
C(12)	0.39354 (88)	0.41788 (71)	0.36512 (59)	
N(1)	0.34368 (47)	0.38133 (43)	0.25079 (38)	
N(2)	0.22189 (68)	−0.22623 (60)	0.42653 (54)	
O(1)	0.41127 (39)	0.16249 (35)	0.22611 (35)	
O(2)	0.13072 (38)	0.25444 (36)	0.14192 (30)	
O(3)	0.27169 (43)	0.23385 (38)	0.37396 (31)	
O(4)	0.21420 (62)	−0.33819 (46)	0.41724 (49)	
O(5)	0.25671 (92)	−0.17487 (58)	0.51376 (49)	
Si	0.26511 (14)	0.20278 (15)	0.24777 (12)	
H(1)	0.5648 (64)	0.2293 (63)	0.1723 (53)	8.53 (166)
H(2)	0.5770 (100)	0.2543 (89)	0.3007 (85)	14.40 (247)
H(3)	0.3240 (159)	0.4059 (141)	0.0906 (119)	18.23 (378)
H(4)	0.5198 (108)	0.4226 (94)	0.2443 (91)	17.64 (262)
H(5)	0.0109 (94)	0.4087 (83)	0.0680 (75)	15.39 (221)
H(6)	0.1575 (70)	0.3782 (64)	0.0215 (52)	8.90 (172)
H(7)	0.1768 (131)	0.4869 (127)	0.2645 (112)	23.05 (327)
H(8)	0.2505 (91)	0.5467 (85)	0.1350 (72)	13.21 (259)
H(9)	0.3551 (89)	0.3513 (82)	0.5073 (70)	12.50 (213)
H(10)	0.2375 (136)	0.3977 (121)	0.4175 (106)	21.79 (274)
H(11)	0.5212 (127)	0.3697 (117)	0.3590 (105)	12.72 (316)
H(12)	0.3843 (109)	0.4923 (102)	0.3738 (83)	16.48 (279)
H(13)	0.0934 (94)	0.0381 (94)	0.0737 (78)	16.49 (227)
H(14)	0.0328 (91)	−0.1812 (79)	0.0594 (71)	14.15 (219)
H(15)	0.0791 (61)	−0.3311 (56)	0.2384 (48)	6.88 (181)
H(16)	0.2816 (66)	0.0046 (63)	0.4139 (55)	9.54 (167)

Atom	Thermal parameters β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.00868 (66)	0.00658 (53)	0.00708 (47)	0.00007 (47)	0.00448 (47)	0.00122 (41)
C(2)	0.01572 (97)	0.00827 (70)	0.00764 (55)	−0.00265 (64)	0.00215 (56)	−0.00057 (50)
C(3)	0.01328 (91)	0.00869 (73)	0.01014 (68)	−0.00195 (63)	0.00217 (62)	−0.00090 (56)
C(4)	0.01035 (72)	0.00910 (67)	0.00859 (56)	−0.00038 (60)	0.00422 (53)	−0.00075 (54)
C(5)	0.01087 (75)	0.00719 (59)	0.00835 (54)	0.00194 (52)	0.00678 (53)	0.00199 (45)
C(6)	0.01277 (83)	0.00708 (62)	0.00788 (52)	0.00053 (54)	0.00519 (52)	0.00077 (44)
C(7)	0.01072 (80)	0.01044 (75)	0.01481 (80)	−0.00306 (62)	0.00776 (65)	−0.00139 (61)
C(8)	0.02105 (132)	0.00892 (83)	0.02318 (121)	−0.00477 (84)	0.01464 (105)	−0.00214 (82)
C(9)	0.01618 (96)	0.00690 (62)	0.00705 (51)	−0.00099 (60)	0.00291 (57)	0.00153 (47)
C(10)	0.02083 (127)	0.00913 (80)	0.01127 (72)	−0.00090 (80)	−0.00013 (73)	0.00167 (64)
C(11)	0.02246 (123)	0.00881 (75)	0.00769 (58)	−0.00428 (74)	0.00608 (68)	−0.00260 (53)
C(12)	0.02892 (150)	0.01051 (86)	0.00902 (66)	−0.00664 (89)	0.00755 (81)	−0.00264 (61)
N(1)	0.01030 (61)	0.00746 (48)	0.00655 (40)	−0.00208 (44)	0.00438 (40)	−0.00062 (35)
N(2)	0.02341 (107)	0.00983 (77)	0.00966 (58)	0.00201 (67)	0.00820 (65)	0.00178 (51)
O(1)	0.01005 (49)	0.00643 (38)	0.01122 (41)	−0.00063 (34)	0.00552 (36)	−0.00103 (31)
O(2)	0.01020 (48)	0.00771 (40)	0.00640 (30)	−0.00070 (34)	0.00140 (31)	0.00107 (29)
O(3)	0.01662 (62)	0.00819 (45)	0.00586 (31)	−0.00197 (40)	0.00444 (36)	−0.00030 (30)
O(4)	0.03002 (103)	0.00588 (47)	0.01662 (62)	0.00400 (53)	0.01242 (64)	0.00327 (43)
O(5)	0.06331 (207)	0.01249 (72)	0.00729 (49)	−0.00270 (93)	0.00847 (80)	0.00055 (48)
Si	0.00786 (17)	0.00579 (13)	0.00507 (11)	−0.00076 (14)	0.00294 (11)	0.00019 (11)

[a] Numbers in parentheses are estimated standard deviations from the least-squares refinement; $\times 10^4$ for hydrogen coordinates, $\times 10^3$ for hydrogen isotropic thermal parameters, and $\times 10^5$ for all other coordinates.

ward the nitrogen atom. Ideally, silicon would be in the plane of the oxygens, but here it is 0.17 Å out of plane, toward the phenyl ring.

The top view of the molecule in Figure 2 clearly shows that in the five-membered bridging rings the carbon atoms bonded to nitrogen are considerably out of plane with respect to the other four atoms. The least-squares fit was therefore made with those four atoms and the deviations from the planes are 0.50, 0.51, and 0.42 Å for atoms C(8), C(10), and C(12), respectively. We had previously observed that these three atoms are disordered in structure I in such a way that two possible conformations are available to the five-membered rings with only those carbons being significantly affected by the disorder.[2] In the *m*-nitro derivative this conformational change does not occur (in the solid state) and the structure is ordered. However, the thermal ellipsoids for these three atoms (Figure 1 and

Table II. Bond Distances and Angles^{a,b}

Bond	Distances, Å	Bond	Distances, Å
Si-C(1)	1.904 (9)	C(7)-H(1)	1.00 (12)
Si-O(1)	1.656 (6)	C(7)-H(2)	0.94 (17)
Si-O(2)	1.661 (6)	C(8)-H(3)	1.56 (20)
Si-O(3)	1.650 (6)	C(8)-H(4)	0.93 (19)
Si-N(1)	2.116 (8)	C(9)-H(5)	1.18 (15)
		C(9)-H(6)	1.11 (13)
O(1)-C(7)	1.426 (11)	C(10)-H(7)	1.29 (17)
C(7)-C(8)	1.527 (18)	C(10)-H(8)	1.30 (18)
C(8)-N(1)	1.461 (14)	C(11)-H(9)	1.03 (14)
		C(11)-H(10)	0.86 (19)
O(2)-C(9)	1.425 (11)	C(12)-H(11)	1.42 (19)
C(9)-C(10)	1.503 (15)	C(12)-H(12)	0.84 (21)
C(10)-N(1)	1.483 (13)		
		C(2)-H(13)	0.81 (18)
O(3)-C(11)	1.437 (11)	C(3)-H(14)	0.96 (17)
C(11)-C(12)	1.503 (14)	C(4)-H(15)	1.28 (10)
C(12)-N(1)	1.447 (12)	C(6)-H(16)	1.04 (15)
C(1)-C(2)	1.396 (13)		
C(2)-C(3)	1.408 (14)		
C(3)-C(4)	1.371 (14)		
C(4)-C(5)	1.360 (13)		
C(5)-C(6)	1.428 (13)		
C(6)-C(1)	1.380 (12)		
C(5)-N(2)	1.472 (12)		
N(2)-O(4)	1.239 (11)		
N(2)-O(5)	1.203 (12)		

Angle	Degrees
C(1)-Si-O(1)	94.96 (33)
C(1)-Si-O(2)	95.96 (35)
C(1)-Si-O(3)	96.56 (35)
N(1)-Si-O(1)	84.51 (29)
N(1)-Si-O(2)	83.46 (31)
N(1)-Si-O(3)	84.43 (31)
O(1)-Si-O(2)	118.51 (34)
O(2)-Si-O(3)	118.92 (35)
O(3)-Si-O(1)	119.38 (35)
Bridge Ring 1	
Si-O(1)-C(7)	122.12 (64)
O(1)-C(7)-C(8)	109.13 (83)
O(1)-C(7)-H(1)	113.4 (72)
O(1)-C(7)-H(2)	105.5 (143)
H(1)-C(7)-C(8)	107.4 (72)
H(2)-C(7)-C(8)	105.4 (149)
H(1)-C(7)-H(2)	115.6 (160)
C(7)-C(8)-N(1)	105.88 (103)
C(7)-C(8)-H(3)	125.6 (77)
C(7)-C(8)-H(4)	100.8 (119)
H(3)-C(8)-N(1)	84.6 (74)
H(4)-C(8)-N(1)	100.2 (132)
H(3)-C(8)-H(4)	130.4 (140)
C(8)-N(1)-Si	105.55 (65)
N(1)-Si-O(1)	84.34 (29)
Phenyl Ring	
C(1)-C(2)-C(3)	121.71 (102)
C(1)-C(2)-H(13)	133.3 (138)
H(13)-C(2)-C(3)	104.7 (138)
C(2)-C(3)-C(4)	122.30 (104)
C(2)-C(3)-H(14)	108.2 (101)
H(14)-C(3)-C(4)	129.4 (100)
C(3)-C(4)-C(5)	115.34 (101)
C(3)-C(4)-H(15)	128.4 (45)
H(15)-C(4)-C(5)	116.3 (45)

Angle	Degrees
Bridge Ring 2	
Si-O(2)-C(9)	123.03 (57)
O(2)-C(9)-C(10)	108.23 (81)
O(2)-C(9)-H(5)	107.8 (98)
O(2)-C(9)-H(6)	116.1 (110)
H(5)-C(9)-C(10)	108.7 (100)
H(6)-C(9)-C(10)	111.3 (115)
H(5)-C(9)-H(6)	104.4 (135)
C(9)-C(10)-N(1)	106.41 (91)
C(9)-C(10)-H(7)	119.4 (82)
C(9)-C(10)-H(8)	105.5 (112)
H(7)-C(10)-N(1)	98.6 (80)
H(8)-C(10)-N(1)	114.0 (108)
H(7)-C(10)-H(8)	112.9 (142)
C(10)-N(1)-Si	104.90 (59)
N(1)-Si-O(2)	83.74 (31)
Bridge Ring 3	
Si-O(3)-C(11)	122.53 (60)
O(3)-C(11)-C(12)	109.04 (82)
O(3)-C(11)-H(9)	114.4 (73)
O(3)-C(11)-H(10)	114.4 (120)
H(9)-C(11)-C(12)	113.8 (78)
H(10)-C(11)-C(12)	106.4 (131)
H(9)-C(11)-H(10)	98.3 (156)
C(11)-C(12)-N(1)	108.50 (85)
C(11)-C(12)-H(11)	122.1 (72)
C(11)-C(12)-H(12)	107.3 (108)
H(11)-C(12)-N(1)	80.8 (78)
H(12)-C(12)-N(1)	113.2 (116)
H(11)-C(12)-H(12)	121.3 (129)
C(12)-N(1)-Si	105.82 (63)
N(1)-Si-O(3)	84.14 (31)

Table II (*Continued*)

Angle	Degrees	Angle	Degrees
Phenyl Ring			
C(4)-C(5)-C(6)	124.68 (94)	Phenyl Ring	
C(4)-C(5)-N(2)	118.32 (93)		
N(2)-C(5)-C(6)	116.99 (92)	C(6)-C(1)-C(2)	116.85 (87)
		C(6)-C(1)-Si	121.93 (70)
O(4)-N(2)-O(5)	123.20 (106)	Si-C(1)-C(2)	120.88 (71)
O(4)-N(2)-C(5)	117.92 (100)		
O(5)-N(2)-C(5)	118.85 (102)	Angles about Bridging Nitrogen	
C(5)-C(6)-C(1)	119.09 (89)	C(8)-N(1)-C(10)	112.04 (104)
C(5)-C(6)-H(16)	119.0 (120)	C(10)-N(1)-C(12)	110.88 (92)
H(16)-C(6)-C(1)	121.9 (122)	C(12)-N(1)-C(8)	116.62 (94)

[a] Standard deviations for bond distances, $\times 10^3$ in the left column and $\times 10^2$ in the right column, given in parentheses were obtained from the variance–covariance matrix calculated during the last cycle of least-squares refinement. [b] Standard deviations for angles, ×10 or ×100 as needed to give an integer, are given in parentheses and were obtained from the variance–covariance matrix calculated during the last cycle of least-squares refinement.

Table III. Equations of Planes in *m*-Nitrophenyl Derivative[a]

Plane	M1	M2	M3	*D*	Rms deviation, Å
Bridge ring 1	1.1276	−0.8744	11.5450	2.9617	0.0218
Bridge ring 2	7.5177	−3.3632	−10.5777	−1.3361	0.0280
Bridge ring 3	8.6802	−3.6159	0.9134	1.8189	0.0260
Oxygens	3.7624	10.2169	−1.3792	2.8957	
C bonded to N	3.6878	10.2516	−1.4802	5.1948	
Nitro group	10.0838	−0.3774	−3.8026	0.7010	
Phenyl ring	9.6615	−3.0591	−5.4476	0.4437	0.0065

[a] The expressions is $(M1)x + (M2)y + (M3)z = D$ where D is the origin to plane distance.

Table IV. Dihedral Angles of Interest

Plane or line	Plane or line	Angle, deg
Bridge ring 1	Bridge ring 2	118.78
Bridge ring 2	Bridge ring 3	120.37
Bridge ring 3	Bridge ring 1	120.75
Bridge ring 1	Phenyl ring	92.03
Bridge ring 2		31.57
Bridge ring 3		28.92
Plane of oxygens		84.50
Plane of C bonded to N		84.90
Plane of nitro group		16.63
Si-C-N- line		5.03
Bridge ring 1	Plane of C bonded to N	91.15
Bridge ring 2		91.20
Bridge ring 3		89.25
Plane of oxygens		0.77
Si-C-N line		89.37
Bridge ring 1	Plane of oxygens	90.45
Bridge ring 2		91.20
Bridge ring 3		88.58
Si-C-N line		89.50

Table V. Root-Mean-Square Thermal Displacements along Principal Axes (A)[a]

Atom	Axis 1	Axis 2	Axis 3
C(1)	0.163 (14)	0.200 (14)	0.242 (12)
C(2)	0.206 (15)	0.243 (15)	0.293 (14)
C(3)	0.211 (16)	0.257 (15)	0.296 (14)
C(4)	0.206 (16)	0.232 (15)	0.259 (12)
C(5)	0.155 (15)	0.194 (14)	0.280 (13)
C(6)	0.202 (16)	0.212 (13)	0.259 (12)
C(7)	0.151 (15)	0.272 (16)	0.336 (16)
C(8)	0.194 (18)	0.270 (17)	0.428 (20)
C(9)	0.186 (17)	0.240 (13)	0.284 (14)
C(10)	0.228 (17)	0.260 (15)	0.375 (17)
C(11)	0.195 (18)	0.241 (13)	0.334 (15)
C(12)	0.216 (20)	0.251 (15)	0.383 (16)
N(1)	0.175 (14)	0.208 (11)	0.246 (10)
N(2)	0.225 (17)	0.251 (11)	0.335 (13)
O(1)	0.194 (10)	0.197 (10)	0.292 (9)
O(2)	0.200 (10)	0.208 (9)	0.255 (8)
O(3)	0.199 (10)	0.216 (9)	0.282 (8)
O(4)	0.174 (12)	0.297 (10)	0.396 (11)
O(5)	0.221 (12)	0.277 (14)	0.549 (14)
Si	0.165 (1)	0.195 (1)	0.202 (1)
H(1)	0.329		
H(2)	0.427		
H(3)	0.481		
H(4)	0.473		
H(5)	0.441		
H(6)	0.336		
H(7)	0.540		
H(8)	0.409		
H(9)	0.398		
H(10)	0.525		
H(11)	0.401		
H(12)	0.457		
H(13)	0.456		
H(14)	0.423		
H(15)	0.295		
H(16)	0.348		

[a] Estimated standard deviations, $\times 10^3$, in parentheses are calculated from the variance–covariance matrix calculated during the last cycle of least-squares refinement.

Table V) show markedly anisotropic thermal motion in a direction perpendicular to the planes of the rings, suggestive of the origin of the disorder in the earlier structure. Bond distances are normal in these rings, and the average C–N–Si, N–C–C, and C–C–O angles of 105.4°, 106.9°, and 108.8°, respectively, are close to the normal tetrahedral value.

The orientation of the phenyl ring with respect to the bridging rings (Figure 2) is such that its plane is very nearly perpendicular to the plane of the O(1) bridge and forms angles of 31.6° and 28.9° to the planes of the O(2) and O(3) bridge rings, respectively, presumably to minimize second-neighbor C–O interactions. Distances in the phenyl ring are normal, but the angle at the

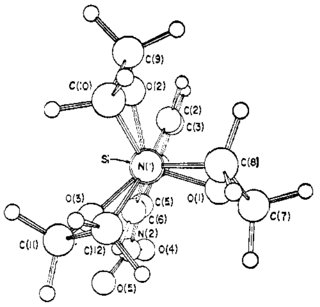

Figure 2. Top view of *m*-nitrophenyl(2,2′,2′′-nitrilotriethoxy)silane looking down the N–Si–C axis.

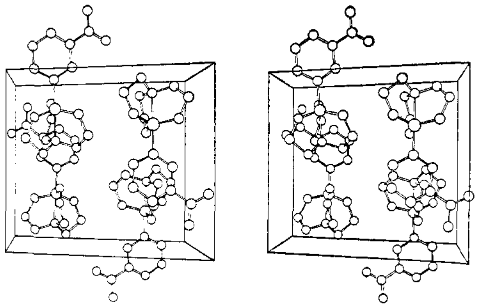

Figure 3. Stereo view of molecular packing in *m*-nitrophenyl(2,2′,2′′-nitrilotriethoxy)silane.

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.

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

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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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