Crystal and Molecular Structure of [Iminobis(ethyleneoxy)]diphenylsilane: a Five-co-ordinate Silicon Compound

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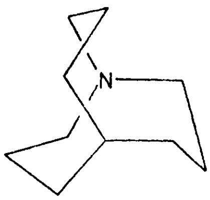
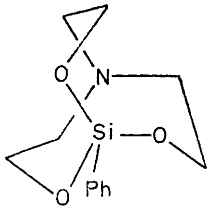
Crystals of the title compound (V) are orthorhombic, space group $P2_12_12_1$, with a = 9·056(7), b = 11·904(10), c = 14·175(13) Å. Monochromated diffractometer data for 1341 planes were used to solve the structure by Patterson and Fourier methods and were refined by least squares to a final R of 0·070. The formal eight-membered ring is bridged by a silicon–nitrogen bond of 2·301 (6) Å, and the silicon atom adopts a trigonal bipyramidal geometry of approximate symmetry C_s.

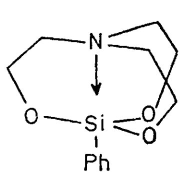
THE existence of five-co-ordinate organosilicon compounds, in which the fifth co-ordination site at the trigonal bipyramidal silicon atom is occupied by a nitrogen atom acting as a σ donor, is now well established.[1-4] A typical example[1] is (III), which may be regarded as a manxine[5] (I) (1-aza-manxane)[6] analogue with a 1,5-ring-closure forming the silicon–nitrogen bond. A Dreiding model of this molecule without the silicon–nitrogen bond, (II), based on the known structure[7] of manxine hydrochloride, may be constructed with symmetry C_3 and with the eight-membered ring in the boat-chair (BC) form. This model has the nitrogen and silicon atoms on the three-fold axis, 3·4 Å apart, and conveniently arranged for interaction between the empty silicon *d* orbitals and the nitrogen atom. Moreover, intramolecular repulsions between hydrogen atoms would tend to decrease the silicon–nitrogen distance in (II) since a similar effect is observed in manxine hydrochloride. These repulsions are not found in a model of



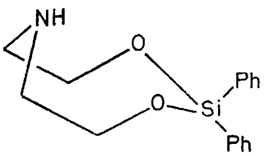
(I)



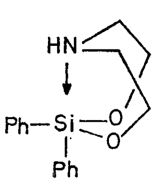
(II)



(III)



(IV)



(V)

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[1] J. W. Turley and F. P. Boer, *J. Amer. Chem. Soc.*, 1968, **90**, 4026.

[2] F. P. Boer, J. W. Turley, and J. J. Flynn, *J. Amer. Chem. Soc.*, 1968, **90**, 5102.

[3] J. W. Turley and F. P. Boer, *J. Amer. Chem. Soc.*, 1969, **91**, 4129.

[4] F. P. Boer and J. W. Turley, *J. Amer. Chem. Soc.*, 1969, **91**, 4134.

[5] J. C. Coll, D. R. Crist, M. C. G. Barrio, and N. J. Leonard, *J. Amer. Chem. Soc.*, 1972, **94**, 7092.

[6] M. Doyle, W. Parker, P. A. Gunn, J. Martin, and D. D. MacNicol, *Tetrahedron Letters*, 1970, 3619.

[7] A. H.-J. Wang, R. J. Missavage, S. R. Byrn, and I. C. Paul, *J. Amer. Chem. Soc.*, 1972, **94**, 7100.

(III). Recently Fink[8] has synthesised $Ph_2Si(OCH_2{\cdot}CH_2)_2NH$ and a model of this, (IV), may be constructed with a BC eight-membered ring of symmetry C_s which is free from the constraints found in (II). Nevertheless, chemical and spectroscopic evidence suggested[8] that a silicon–nitrogen bond is present and that the molecule is best described as (V). We have therefore carried out an X-ray analysis on $Ph_2Si(OCH_2{\cdot}CH_2)_2NH$ to verify the other evidence and to establish the geometrical features of the molecule.

EXPERIMENTAL

Crystal Data.—$C_{16}H_{19}NO_2Si$, $M = 285{\cdot}4$, Orthorhombic, $a = 9{\cdot}056(7)$, $b = 11{\cdot}904(10)$, $c = 14{\cdot}175(13)$ Å, $U = 1528{\cdot}1$ Å^3, $D_m = 1244$, $Z = 4$, $D_c = 1240$ kg m^{-3}. Space group $P2_12_12_1$ (D_2^4, No. 19), Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 157 m^{-1}.

Unit-cell dimensions were obtained from zero-layer precession photographs by a least-squares process; the standard deviations are estimates to allow for systematic errors which are expected to be much larger than the random errors. Intensity data were collected round a on a Hilger and Watts linear diffractometer fitted with a graphite monochromator. The limit switches on the machine were set to operate when θ was 26° and 1341 intensities $> 2\sigma$ were used in the analysis.

Structure Determination and Refinement.—The structure was solved from the three-dimensional Patterson function with the assistance of a Fourier map based on the phases of the silicon atom. This trial structure was refined by a least-squares block-diagonal process with 3 × 3 and 1 × 1 or, later, 6 × 6 matrices for the co-ordinates and temperature factors with $w^{-1} = 2{\cdot}9 + |F_o| + 0{\cdot}01|F_o|^2$. Hydrogen atom positions were calculated and checked with a three-dimensional difference synthesis when R was 0·091. There was good agreement for the nitrogen and phenyl hydrogen atoms, but the methylene hydrogen atoms could not be identified clearly in the difference map. The temperature factors of the methylene carbon atoms were rather high, approximate root-mean-square displacements of 0·31—0·38 Å, so disorder was suspected. Another difference map was then calculated, without any contribution from the methylene carbon atoms, and examined for disorder in these groups. Significant electron density was only found where the methylene carbons had previously been placed. These atoms were then put back and refinement of the positional parameters of all atoms continued till R was 0·070. Isotropic temperature factors for the hydrogen atoms were fixed at 0·01 units of U higher than the carbon atoms to which they are bonded.

RESULTS AND DISCUSSION

The results of the analysis are summarized in Tables 1—3, atomic co-ordinates are listed in Table 1, atomic thermal parameters in Table 2, and bond lengths and angles in Table 3. Figure 1 shows the molecule projected down the a axis and the labelling of the atoms: Figure 2 shows the molecule projected down the Si–N bond. Final values of the structure factors are listed in Supplementary Publication No. SUP 21038 (10 pp., 1 microfiche).*

The analysis confirms that the molecule has the bicyclic form (V) with nitrogen bonded to silicon. The molecule is asymmetric, and therefore chiral, so that individual crystals are built up from one optical isomer only (space group $P2_12_12_1$). However, the large thermal motion, especially that of the phenyl and methylene groups, suggests that the energy barrier for the inter-

TABLE 1

Final atomic co-ordinates (Å) with standard deviations in parentheses

Atom	X	Y	Z
Si	1·3881(16)	0·9599(16)	1·3516(15)
O(1)	0·1577(47)	0·1058(51)	0·6730(43)
O(2)	1·6341(51)	2·5642(44)	1·0066(46)
N	2·1791(56)	0·7681(69)	−0·8011(56)
C(1)	0·5612(61)	1·1746(62)	3·0493(57)
C(2)	−0·1835(78)	0·1332(82)	3·6222(75)
C(3)	−0·7205(84)	0·2111(105)	4·8973(83)
C(4)	−0·5040(88)	1·3515(103)	5·6681(80)
C(5)	0·2222(106)	2·3642(94)	5·1492(82)
C(6)	0·7632(92)	2·2853(77)	3·8474(73)
C(7)	2·9404(62)	−0·0004(73)	1·8257(55)
C(8)	2·9321(100)	−1·3704(75)	1·9759(76)
C(9)	4·1222(130)	−1·9979(110)	2·3479(84)
C(10)	5·2565(115)	−1·3048(158)	2·5573(98)
C(11)	5·2733(92)	0·0534(164)	2·4249(96)
C(12)	4·1365(77)	0·6874(100)	2·0769(77)
C(13)	0·1055(119)	−0·3109(141)	−0·6833(87)
C(14)	1·1896(128)	0·0169(179)	−1·4480(87)
C(15)	2·2268(119)	3·0423(117)	−0·1766(95)
C(16)	2·2321(173)	2·1336(118)	−1·2580(107)
HN	2·99(10)	0·45(9)	−0·79(10)
H(2)	−0·43(9)	−0·56(9)	3·22(10)
H(3)	−1·20(11)	−0·50(9)	5·52(10)
H(4)	−0·66(12)	1·60(10)	6·55(10)
H(5)	0·35(11)	3·47(10)	5·58(11)
H(6)	1·01(11)	3·19(9)	3·47(11)
H(8)	2·10(11)	−1·95(10)	2·02(11)
H(9)	3·94(12)	−2·66(10)	2·45(10)
H(10)	6·07(16)	−1·72(13)	3·00(14)
H(11)	6·09(14)	0·62(12)	2·59(12)
H(12)	4·08(11)	1·79(10)	2·02(10)
H(13A)	0·02(14)	−1·22(11)	−0·59(13)
H(13B)	−0·53(14)	−0·35(12)	−0·82(13)
H(14A)	1·82(15)	−0·30(13)	−1·47(14)
H(14B)	1·07(17)	0·04(15)	−2·31(12)
H(15A)	3·13(13)	3·05(13)	0·06(14)
H(15B)	2·03(12)	4·11(11)	−0·38(11)
H(16A)	3·10(15)	1·92(16)	−1·51(15)
H(16B)	1·42(15)	2·37(13)	−1·61(14)

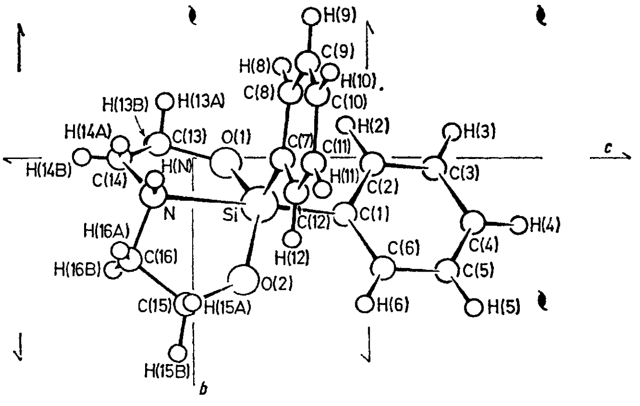

FIGURE 1 The molecule projected down the a axis and the labelling of the atoms

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[8] W. Fink, personal communication; the compound was prepared in the course of studies of biologically active organosilicon compounds.

TABLE 2

Temperature factors (Å² × 10⁴) *

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$	Atom	U
Si	412(9)	482(9)	335(8)	105(20)	−31(19)	−66(19)	HN	735
O(1)	524(32)	822(40)	406(28)	−106(64)	−285(59)	−63(55)	H(2)	739
O(2)	711(40)	582(35)	490(31)	4(65)	122(54)	157(60)	H(3)	902
N	557(42)	965(59)	382(31)	358(93)	94(80)	76(64)	H(4)	953
C(1)	444(40)	584(49)	318(33)	210(75)	−100(69)	−113(67)	H(5)	954
C(2)	590(49)	822(60)	505(45)	−292(101)	66(94)	81(86)	H(6)	770
C(3)	600(58)	1134(87)	671(59)	−217(130)	140(127)	134(105)	H(8)	872
C(4)	743(63)	1331(91)	486(51)	865(132)	28(118)	315(110)	H(9)	1127
C(5)	1009(86)	978(77)	575(60)	104(153)	−515(123)	−56(132)	H(10)	1477
C(6)	903(67)	630(54)	476(49)	4(117)	−132(91)	11(105)	H(11)	1279
C(7)	523(48)	758(52)	254(32)	320(90)	152(75)	−76(74)	H(12)	896
C(8)	1087(88)	719(57)	511(53)	945(130)	−133(96)	−307(122)	H(13A)	1271
C(9)	1476(130)	1049(98)	557(58)	1248(201)	−188(137)	−125(157)	H(13B)	1271
C(10)	857(88)	2586(193)	689(71)	1506(227)	1101(198)	−16(134)	H(14A)	1511
C(11)	529(62)	2247(177)	761(76)	370(185)	768(205)	20(124)	H(14B)	1511
C(12)	535(51)	1251(93)	602(58)	−58(127)	651(135)	−363(97)	H(15A)	1043
C(13)	1099(98)	1894(148)	519(54)	−848(223)	−1040(159)	−58(134)	H(15B)	1043
C(14)	1219(113)	2516(201)	499(66)	−1449(286)	−1197(203)	487(159)	H(16A)	1542
C(15)	1203(104)	996(79)	629(67)	−213(172)	633(128)	410(145)	H(16B)	1542
C(16)	2449(240)	956(91)	862(86)	836(268)	541(164)	1797(261)		

* For heavy atoms (with standard deviations in parentheses), in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})]$; for hydrogens: $\exp[-2\pi^2Us^2]$, $s = (2\sin\theta)/\lambda$.

TABLE 3

Bond lengths (Å) and angles (°), with standard deviations in parentheses

(*a*) Bond lengths

To Si		Ph groups	
Si–C(1)	1·901(6)	C(1)–C(2)	1·403(10)
Si–C(7)	1·886(7)	C(2)–C(3)	1·386(12)
Si–N	2·301(6)	C(3)–C(4)	1·393(13)
Si–O(1)	1·644(5)	C(4)–C(5)	1·350(13)
Si–O(2)	1·659(5)	C(5)–C(6)	1·412(13)
		C(6)–C(1)	1·383(10)
Oxygen–Carbon		C(7)–C(8)	1·378(11)
O(1)–C(13)	1·420(13)	C(8)–C(9)	1·396(14)
O(2)–C(15)	1·407(12)	C(9)–C(10)	1·346(17)
		C(10)–C(11)	1·365(18)
Nitrogen–Carbon		C(11)–C(12)	1·347(15)
N–C(14)	1·401(15)	C(12)–C(7)	1·402(11)
N–C(16)	1·441(15)	Mean C $\overset{\cdots\cdot}{-}$ C	1·380
C(sp^3)–C(sp^3)		C(sp^2)–H	
C(13)–C(14)	1·367(18)	Average	0·99(12)
C(15)–C(16)	1·413(18)		
C(sp^3)–H			
Average	0·88(15)		
N–H	0·87(9)		

(*b*) Bond angles

At Si		In Ph groups	
C(1)–Si–C(7)	101·0(3)	C(1)–C(2)–C(3)	122·7(7)
C(1)–Si–O(1)	95·8(3)	C(2)–C(3)–C(4)	119·7(8)
C(1)–Si–O(2)	98·1(3)	C(3)–C(4)–C(5)	119·0(9)
C(1)–Si–N	174·0(3)	C(4)–C(5)–C(6)	121·2(9)
N–Si–C(7)	84·8(3)	C(5)–C(6)–C(1)	121·4(7)
N–Si–O(1)	80·1(2)	C(6)–C(1)–C(2)	116·0(6)
N–Si–O(2)	80·5(2)		
C(7)–Si–O(1)	117·1(3)	C(7)–C(8)–C(9)	118·1(8)
C(7)–Si–O(2)	115·0(3)	C(8)–C(9)–C(10)	121·9(10)
O(1)–Si–O(2)	121·8(3)	C(9)–C(10)–C(11)	120·5(12)
		C(10)–C(11)–C(12)	118·9(11)
Five-membered rings		C(11)–C(12)–C(7)	122·4(9)
Si–O(1)–C(13)	125·0(6)	C(12)–C(7)–C(8)	118·2(7)
Si–O(2)–C(15)	124·5(6)		
O(1)–C(13)–C(14)	115·8(10)		
O(2)–C(15)–C(16)	115·3(10)		
C(13)–C(14)–N	115·5(11)		
C(15)–C(16)–N	111·5(10)		
C(14)–N–Si	103·5(6)		
C(16)–N–Si	103·3(6)		
N–Si–O(1)	80·1(2)		
N–Si–O(2)	80·5(2)		
Other			
C(14)–N–C(16)	112·8(9)		

conversion of the two forms is low (*cf.* Figure 2), and that in solution the molecule may well adopt the average symmetry C_s.

The ligands round the silicon atom form a trigonal bipyramid which approximates closely to the symmetry C_s (see Table 3). The silicon–nitrogen bond length [2·301(6) Å] fits nicely into the simple bonding scheme proposed by Boer and Turley:[4] it is longer than that found[1] in (III), but less than that in (VI).[4] Although the local symmetry at silicon is only C_s, the silicon–carbon bond lengths have the correct relative magnitudes, axial longer than equatorial, expected for D_{3h} symmetry.[9] These lengths, [ax. 1·906(6) and eq. 1·886(7) Å], are greater than those found in four-co-ordinate organosilicon compounds, *e.g.* 1·843(5) in $PhSiH_3$,[10] and

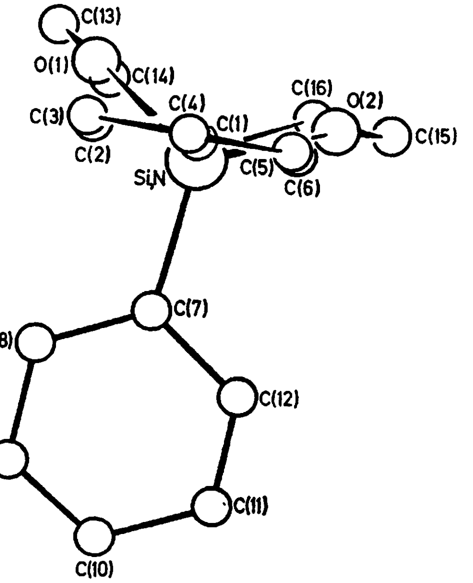

FIGURE 2 The molecule projected down the silicon–nitrogen bond: hydrogen atoms have been omitted for clarity

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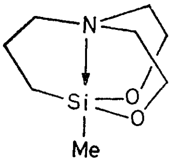
[9] F. A. Cotton, *J. Chem. Phys.*, 1961, **35**, 228.

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

1·876(4) Å in Ph_4Si,[11] but they are close to the value found in (III)[1] [1·882(6) Å]. Curiously enough they tend to be longer than the Si–C(sp^3) bond lengths [ax. 1·877(5) and eq. 1·898(5) Å] in (VI),[4] which also has local symmetry C_s at silicon, but the Si–C equatorial bond is longer than the axial one.



(VI)

The silicon–oxygen bond lengths lie in the range of values found in related compounds[1-4] and are a little longer than those in aliphatic phenyl ethers.[12] The considerable thermal motion of the carbon atoms not bonded to silicon leads to artificially low values for the C–C, C⋯C, C–N, and C–O bond lengths.

One of the five-membered rings is almost planar, with torsion angles: −1·4(7) O(1)–C(13), 2·5(4) C(13)–C(14), −2·3(7) C(14)–N, 1·3(7) N–Si, and 0·0(7) Si–O(1). The second is in a twisted envelope form in which no four consecutive atoms are coplanar, the torsion angles are: −19·1(7) N–C(16), 25·3(4) C(16)–C(15), −19·3(10) C(15)–O(2), 5·3 O(2)–Si, and 8·3(9) Si–N. The large thermal motion of the ethylene groups suggests that these five-membered rings are not rigid. The co-ordination around the nitrogen atom is approximately tetrahedral with the lone pair electrons occupying an axial site of the trigonal bipyramidal nitrogen atom.

The van der Waals contacts present no evidence for hydrogen bond formation of the N–H ⋯ O type; the shortest contacts found for the various types are: 2·76 O ⋯ H, 2·74 C ⋯ H, 2·30 H ⋯ H, and 3·51 Å for C ⋯ N.

We thank Dr. W. Fink who suggested the problem, supplied the crystals, and measured the density.

[4/291 *Received, 14th February*, 1974]

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[11] C. Glidewell and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1971, 3127.

[12] *Chem. Soc. Special Publ.*, No. 18, 1965.