Structure of the Dimethylsilylamine Pentamer, $(C_2H_9NSi)_5$.* A Redetermination

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Abstract. $M_r = 375 \cdot 8$, $P2_1/m$, $a = 6 \cdot 408$ (8), $b = 19 \cdot 491$ (6), $c = 9 \cdot 467$ (3) Å, $\beta = 90 \cdot 79$ (7)°, $U = 1182$ (3) Å^3, $Z = 2$, $D_x = 1 \cdot 056$ Mg m^{-3}, Mo $K\alpha$ radiation, $\bar\lambda = 0 \cdot 71069$ Å, $\mu = 0 \cdot 298$ mm^{-1}, $T = 118$ K, $F(000) = 420$, $R = 0 \cdot 0504$ for 2698 reflections. The unit cell contains two pentameric, ten-membered rings of alternating N and Si atoms. Each ring lies across a crystallographic mirror plane. All Si–N distances [mean $1 \cdot 976$ (4) Å] are equivalent and greater by *ca* $0 \cdot 26$ Å than that found for the unassociated molecule in the gas phase. The coordination at N and Si is pyramidal and trigonal bipyramidal respectively. The crystal structure consists of essentially isolated rings packed parallel to each other.

Introduction. As part of continuing work in this Department on low-melting silyl compounds, we have redetermined the crystal and molecular structure of dimethylsilylamine. As previously established (Sujishi & Witz, 1954), this compound has an anomalously high melting point (276 K) in comparison with the other members of the homologous series $N(CH_3)_{3-x}(SiH_3)_x (x = 0{-}3)$ $[x = 3$, Barrow & Ebsworth (1984); $x = 0$, Blake, Ebsworth & Welch (1984)], all of which melt around 150 K. The pentameric nature of the present compound was previously established (Rudman, Hamilton, Novick & Goldfarb, 1967), providing an explanation of the anomaly, and simultaneously furnishing the first crystallographic identification of pentacoordinate Si. However, paucity of data prevented satisfactory refinement and the molecular parameters were therefore subject to large uncertainties.

Experimental. Dimethylsilylamine prepared (Sujishi & Witz, 1954), pure by ^{1}H NMR and IR, sealed in Pyrex tube. D_m not determined. Colourless cylindrical crystal, $0 \cdot 04 \times 0 \cdot 04 \times 0 \cdot 05$ cm, grown on low-temperature-equipped Weissenberg goniometer and transferred as described previously (Blake, Cradock, Ebsworth, Rankin & Welch, 1984) to similarly equipped CAD-4 diffractometer, 118 K, 25 reflections ($14 < \theta < 15°$) centred, graphite-monochromated Mo $K\alpha$ radiation. For data collection $\theta_{max} = 30°$, $\omega{-}2\theta$ scan in 96 steps,

ω-scan width $(0 \cdot 8 + 0 \cdot 35 \tan\theta)°$, rapid prescan after which reflections with $I \geq 1 \cdot 0\sigma(I)$ remeasured such that final net intensity had $I > 33\sigma(I)$ subject to maximum measuring time of 90 s. No significant crystal decay or movement. 3515 unique reflections over 76 X-ray hours. No absorption correction. Space group confirmed by refinement. For structure solution and refinement 2698 amplitudes $[F \geq 2 \cdot 0\sigma(F)]$. Automatic centrosymmetric direct methods (Sheldrick, 1976) full-matrix least squares on F, $w^{-1} = [\sigma(F)^2 + 0 \cdot 00269 (F)^2]$, anisotropic thermal parameters for all non-H atoms, all H atoms positionally refined [$U\dagger = 0 \cdot 025$ (silyl) or $0 \cdot 03$ (methyl) Å^2], $R = 0 \cdot 0504$, $wR = 0 \cdot 0656$, data:variable ratio 16:1. $(\Delta/\sigma)_{max}$ in final cycle $< 0 \cdot 03$. Max. peak and min. trough in final ΔF synthesis $0 \cdot 26$ and $-0 \cdot 32$ e Å^{-3} respectively. Neutral-atom scattering factors for C,N,Si (Cromer & Liberman, 1970) and H (Stewart, Davidson & Simpson, 1965). Computer programs *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1976), *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *ORTEP*II (Johnson, 1976).

Discussion. Table 1 lists derived fractional coordinates.‡ The coordinates of the nonhydrogen atoms are in close agreement with those previously found (Rudman, Hamilton, Novick & Goldfarb, 1967). Fig. 1 is a projection of one pentamer onto a plane defined by Si(2), Si(3) and Si(3′), where the last two atoms are related by the mirror plane at $y = 0 \cdot 25$. Table 2 lists interatomic separations and interbond angles.

In the crystal, dimethylsilylamine assumes a highly unusual structure in which N atoms occupy the corners of a pentagon with Si atoms (displaced slightly outward from the centre of the ring) midway along its sides. The crystallographically unique half-pentamers intersect on the line Si(2)⋯N(2) giving an angle of $170 \cdot 48°$ between their least-squares planes. Puckering also

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† The isotropic temperature factor is defined as $\exp[-8\pi^2U(\sin^2\theta/\lambda^2)]$.

‡ Lists of structure factors, anisotropic thermal parameters and least-squares-planes' details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39207 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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* 1,1,3,3,5,5,7,7,9,9-Decamethylcyclopenta-λ^5-sil-λ^4-azane.

Table 1. *Fractional coordinates with standard deviations*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Si(1)	0·81566 (9)	0·11548 (3)	0·61631 (6)	0·0173
Si(2)	0·94724 (12)	0·25000	0·43903 (8)	0·0153
Si(3)	0·55537 (9)	0·16686 (3)	0·88607 (6)	0·0191
N(1)	0·9524 (3)	0·14882 (9)	0·44377 (17)	0·0172
N(2)	0·4435 (4)	0·25000	0·97634 (25)	0·0201
N(3)	0·6744 (3)	0·08572 (9)	0·79066 (19)	0·0215
C(1)	0·8450 (4)	0·11934 (12)	0·31864 (23)	0·0256
C(2)	0·5031 (5)	0·25000	1·1269 (3)	0·0275
C(3)	0·5059 (4)	0·03684 (13)	0·7548 (3)	0·0293
C(4)	1·1727 (4)	0·12680 (12)	0·4451 (3)	0·0244
C(5)	0·8272 (4)	0·05149 (13)	0·8849 (3)	0·0304
C(6)	0·2123 (5)	0·25000	0·9639 (4)	0·0260
HS(11)	0·876 (5)	0·0470 (15)	0·584 (3)	
HS(12)	0·634 (5)	0·1401 (15)	0·564 (3)	
HS(13)	0·959 (5)	0·1559 (15)	0·698 (3)	
HS(21)	1·018 (7)	0·25000	0·316 (4)	
HS(22)	1·056 (7)	0·25000	0·559 (4)	
HS(23)	0·724 (7)	0·25000	0·444 (4)	
HS(31)	0·472 (5)	0·1298 (15)	0·980 (3)	
HS(32)	0·453 (5)	0·1852 (15)	0·755 (3)	
HS(33)	0·758 (5)	0·1918 (15)	0·919 (3)	
H(11)	0·920 (5)	0·1329 (16)	0·230 (3)	
H(12)	0·852 (5)	0·0697 (16)	0·329 (3)	
H(13)	0·703 (5)	0·1366 (16)	0·318 (3)	
H(21)	0·444 (5)	0·2119 (15)	1·181 (3)	
H(22)	0·662 (8)	0·25000	1·144 (4)	
H(31)	0·553 (5)	−0·0019 (16)	0·704 (3)	
H(32)	0·444 (5)	0·0217 (16)	0·835 (3)	
H(33)	0·414 (5)	0·0574 (16)	0·697 (3)	
H(41)	1·174 (5)	0·0835 (18)	0·448 (3)	
H(42)	1·239 (5)	0·1382 (16)	0·361 (3)	
H(43)	1·239 (5)	0·1485 (16)	0·523 (3)	
H(51)	0·782 (5)	0·0426 (16)	0·976 (3)	
H(52)	0·880 (5)	0·0096 (16)	0·847 (3)	
H(53)	0·945 (5)	0·0840 (17)	0·903 (3)	
H(61)	0·154 (5)	0·2113 (15)	1·006 (3)	
H(62)	0·167 (7)	0·25000	0·859 (4)	

Table 2. *Interatomic distances (Å) and angles (°)*

Si(1)—N(1)	1·9744 (18)	N(3)—C(3)	1·476 (3)
Si(1)—N(3)	1·9804 (19)	N(3)—C(5)	1·475 (3)
Si(1)—HS(11)	1·42 (3)	C(1)—H(11)	1·01 (3)
Si(1)—HS(12)	1·35 (3)	C(1)—H(12)	0·97 (3)
Si(1)—HS(13)	1·43 (3)	C(1)—H(13)	0·97 (3)
Si(2)—N(1)	1·9729 (18)	C(2)—H(21)	0·98 (3)
Si(2)—HS(21)	1·25 (3)	C(2)—H(22)	1·03 (4)
Si(2)—HS(22)	1·32 (3)	C(3)—H(31)	0·94 (3)
Si(2)—HS(23)	1·43 (3)	C(3)—H(32)	0·91 (3)
Si(3)—N(2)	1·9717 (20)	C(3)—H(33)	0·90 (3)
Si(3)—N(3)	1·9794 (19)	C(4)—H(41)	0·85 (3)
Si(3)—HS(31)	1·27 (3)	C(4)—H(42)	0·94 (3)
Si(3)—HS(32)	1·44 (3)	C(4)—H(43)	0·95 (3)
Si(3)—HS(33)	1·42 (3)	C(5)—H(51)	0·93 (3)
N(1)—C(1)	1·478 (3)	C(5)—H(52)	0·95 (3)
N(1)—C(4)	1·475 (3)	C(5)—H(53)	1·00 (3)
N(2)—C(2)	1·471 (3)	C(6)—H(61)	0·94 (3)
N(2)—C(6)	1·485 (3)	C(6)—H(62)	1·03 (4)
N(1)—Si(1)—N(3)	177·76 (8)	Si(1)—N(3)—Si(3)	109·26 (9)
N(1)—Si(1)—HS(11)	90·4 (12)	Si(1)—N(3)—C(3)	109·79 (14)
N(1)—Si(1)—HS(12)	88·3 (12)	Si(1)—N(3)—C(5)	109·23 (14)
N(1)—Si(1)—HS(13)	88·5 (12)	Si(3)—N(3)—C(3)	109·60 (14)
N(3)—Si(1)—HS(11)	91·8 (12)	Si(3)—N(3)—C(5)	110·01 (14)
N(3)—Si(1)—HS(12)	90·4 (12)	C(3)—N(3)—C(5)	108·94 (18)
N(3)—Si(1)—HS(13)	90·6 (12)	N(1)—C(1)—H(11)	110·1 (18)
HS(11)—Si(1)—HS(12)	119·4 (17)	N(1)—C(1)—H(12)	106·8 (19)
HS(11)—Si(1)—HS(13)	117·3 (16)	N(1)—C(1)—H(13)	107·5 (19)
HS(12)—Si(1)—HS(13)	123·3 (17)	H(11)—C(1)—H(12)	108·6 (26)
N(1)—Si(2)—HS(21)	90·9 (15)	H(11)—C(1)—H(13)	110·9 (26)
N(1)—Si(2)—HS(22)	88·4 (15)	H(12)—C(1)—H(13)	112·7 (26)
N(1)—Si(2)—N(1')	176·78 (13)	N(2)—C(2)—H(21)	114·1 (18)
N(1)—Si(2)—HS(23)	90·9 (14)	N(2)—C(2)—H(22)	113·4 (21)
HS(21)—Si(2)—HS(22)	126·9 (21)	H(21)—C(2)—H(22)	107·8 (27)
HS(21)—Si(2)—HS(23)	113·8 (21)	N(3)—C(3)—H(31)	113·3 (19)
HS(22)—Si(2)—HS(23)	119·4 (20)	N(3)—C(3)—H(32)	110·2 (20)
N(2)—Si(3)—N(3)	177·76 (8)	N(3)—C(3)—H(33)	109·0 (21)
N(2)—Si(3)—HS(31)	90·3 (13)	H(31)—C(3)—H(32)	107·9 (28)
N(2)—Si(3)—HS(32)	90·3 (12)	H(31)—C(3)—H(33)	105·0 (28)
N(2)—Si(3)—HS(33)	87·8 (12)	H(32)—C(3)—H(33)	111·3 (28)
N(3)—Si(3)—HS(31)	91·9 (13)	N(1)—C(4)—H(41)	107·5 (22)
N(3)—Si(3)—HS(32)	88·8 (12)	N(1)—C(4)—H(42)	111·6 (20)
N(3)—Si(3)—HS(33)	90·9 (12)	N(1)—C(4)—H(43)	107·4 (19)
HS(31)—Si(3)—HS(32)	123·6 (18)	H(41)—C(4)—H(42)	105·2 (29)
HS(31)—Si(3)—HS(33)	115·9 (18)	H(41)—C(4)—H(43)	114·5 (29)
HS(32)—Si(3)—HS(33)	120·5 (17)	H(42)—C(4)—H(43)	110·7 (28)
Si(1)—N(1)—Si(2)	109·89 (8)	N(3)—C(5)—H(51)	115·7 (20)
Si(1)—N(1)—C(1)	109·15 (13)	N(3)—C(5)—H(52)	113·2 (19)
Si(1)—N(1)—C(4)	109·44 (13)	N(3)—C(5)—H(53)	108·2 (19)
Si(2)—N(1)—C(1)	111·28 (13)	H(51)—C(5)—H(52)	107·8 (27)
Si(2)—N(1)—C(4)	107·87 (13)	H(51)—C(5)—H(53)	101·5 (27)
C(1)—N(1)—C(4)	109·18 (17)	H(52)—C(5)—H(53)	109·7 (26)
Si(3)—N(2)—Si(3')	110·55 (11)	N(2)—C(6)—H(61)	111·8 (19)
Si(3)—N(2)—C(2)	109·20 (15)	N(2)—C(6)—H(62)	110·1 (20)
Si(3)—N(2)—C(6)	109·52 (15)	H(61)—C(6)—H(62)	107·8 (28)
C(2)—N(2)—C(6)	108·82 (19)		

occurs elsewhere around the ring; perhaps the best description of the pentamer is as an envelope whose flap is defined by the least-squares plane through N(3), Si(3), N(2), Si(3'), and N(3'). The body of the envelope is defined as the best plane through N(3), Si(1), N(1), Si(2), N(1'), Si(1'), and N(3'). Whereas in the vapour the structure of the isolated N(CH₃)₂SiH₃ molecule is characterized by pyramidal geometries at both N* and Si and by bond lengths of 1·712 (3) and 1·459 (3) Å for N—Si and N—C respectively (Gundersen, Mayo, Rankin & Robertson, 1984) in the solid the Si coordination is trigonal bipyramidal and these distances increase to 1·976 (4) and 1·476 (4) Å respectively (mean values). For the latter, this represents an increase of 0·017 (5) Å, but phase, temperature and N coordination number all change on going from vapour to crystalline solid and so it is difficult to comment authoritatively on the origin of this lengthening which is, anyway, only just statistically significant. The longest and shortest N—C bonds lie on the mirror plane and are directed respectively into and out of the molecular fold: the difference between them is attributable to the differing degrees to which they are required to minimize close contacts between the methyl H atoms

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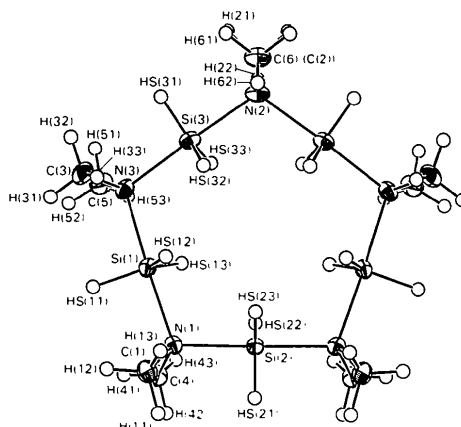* The pyramid at N is flattened, with C—N—C = 112·0 (6) and Si—N—C = 120·7 (3)°.

Fig. 1. The dimethylsilylamine pentamer, with thermal ellipsoids drawn at the 50% electron probability level, except for H atoms which have an artificial radius of 0·1 Å for clarity.
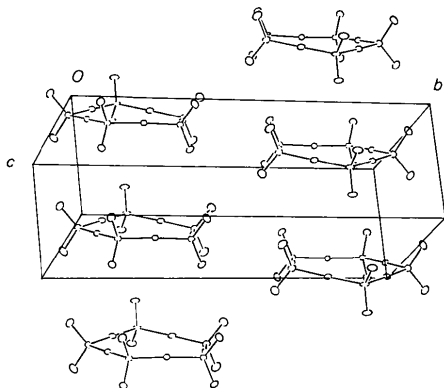
Fig. 2. Crystal packing diagram for dimethylsilylamine. H atoms are omitted for clarity.

and those on Si(3). Within each methyl group, C—H bonds are staggered with respect to N—C and N—Si bonds, but eclipse the C—H bonds of the other methyl group on the same N atom.

In contrast to the original determination of the structure of $[N(CH_3)_2SiH_3]_5$ in the solid phase (Rudman, Hamilton, Novick & Goldfarb, 1967) we have been able to locate accurately and refine H atoms. The disposition of the silyl H atoms – those lying close to the plane of the ring are outside rather than inside it – is governed by H(silyl)$\cdots$H(silyl) repulsions: the opposite arrangement would involve contacts as close as 1·5 Å. Interactions with methyl H atoms are much less critical: in neither arrangement do contacts below 2·27 Å occur, although those found experimentally are on average longer than those calculated for the alternative structure.

There are no significant intermolecular contacts between the individual ten-membered rings which pack parallel to each other (Fig. 2).

Distortions of essentially tetrahedral species by interactions with relatively close neighbouring atoms have been described as incipient S_N2 reactions whose transition state involves trigonal-bipyramidal intermediates (Bürgi, 1973, 1975). In compounds with N—Si

bonds in which no close intermolecular contacts occur, the N—Si distances lie around 1·7 Å, e.g. trisilylamine (Barrow & Ebsworth, 1984). However, involvement of the Si atom in additional intermolecular contacts results in N—Si lengthening, e.g. from 1·704 (4) (gas phase) to 1·720 (6) Å in $(OCN)SiH_3$ (Barrow, Ebsworth & Harding, 1980). This increase is an order of magnitude less than that observed in dimethylsilylamine. In this context the dimethylsilylamine pentamer may therefore be regarded as a 'frozen' assemblage of five molecules in a fully symmetric transition state.

References

BARROW, M. J. & EBSWORTH, E. A. V. (1984). J. Chem. Soc. Dalton Trans. In the press.

BARROW, M. J., EBSWORTH, E. A. V. & HARDING, M. M. (1980). J. Chem. Soc. Dalton Trans. pp. 1839–1844.

BLAKE, A. J., CRADOCK, S., EBSWORTH, E. A. V., RANKIN, D. W. H. R. & WELCH, A. J. (1984). J. Chem. Soc. Dalton Trans. To be published.

BLAKE, A. J., EBSWORTH, E. A. V. & WELCH, A. J. (1984). Acta Cryst. C40, 413–415.

BÜRGI, H.-B. (1973). Inorg. Chem. 12, 2321–2325.

BÜRGI, H.-B. (1975). Angew. Chem. Int. Ed. Engl. 14, 460–473.

CROMER, D. T. & LIBERMAN, D. (1970). J. Chem. Phys. 53, 1891–1898.

GUNDERSEN, G., MAYO, R. A., RANKIN, D. W. H. & ROBERTSON, H. E. (1984). To be published.

JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

ROBERTS, P. & SHELDRICK, G. M. (1976). XANADU. Univ. of Cambridge, England.

RUDMAN, R., HAMILTON, W. C., NOVICK, S. & GOLDFARB, T. D. (1967). J. Am. Chem. Soc. 89, 5157–5160.

SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

SUJISHI, S. & WITZ, S. (1954). J. Am. Chem. Soc. 76, 4631–4636.