Crystal and Molecular Structure of Trisilylamine at 115 K †

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At 115 K, crystals of trisilylamine are triclinic, space group $P\bar{1}$, with $a = 6.84$, $b = 8.17$, $c = 6.87$ Å, $\alpha = 95.5$, $\beta = 119.1$, $\gamma = 98.6°$ (0.3% estimated standard deviations are assumed), and $Z = 2$. Crystals were grown *in situ* on a Weissenberg goniometer fitted with low-temperature equipment. The structure has been refined to $R = 0.051$ using 651 photographic (microdensitometer) intensities. There are no short intermolecular contacts. Deviations from molecular C_{3h} symmetry are negligible, even for the hydrogen atoms. The mean length of the Si–N bonds is 1.730(5) Å. The heavy atoms vibrate mainly in a direction which is parallel to the molecular C_3 axis.

Electron diffraction studies [1] have clearly established that in the *gas* phase trisilylamine [$N(SiH_3)_3$] is monomeric and has a trigonal planar heavy-atom skeleton. This geometry correlates with the sharply reduced basicity of trisilylamine as compared with trimethylamine; $(p \longrightarrow d)$ π bonding between N and Si has been proposed as the most likely explanation for the chemical and stereochemical inactivity of the nitrogen lone pair of electrons in trisilylamine.

Dimethylsilylamine (Me_2NSiH_3) is also monomeric in the gas phase [2] but crystallises in pentameric rings through the formation of $N \cdots Si$ intermolecular interactions that are so short that silicon achieves trigonal-bipyramidal co-ordination.[3] This behaviour may be related to the greater basicity of Me_2NSiH_3 than $N(SiH_3)_3$ and to the non-planar geometry at N in gaseous dimethylsilylamine: both observations imply that the lone pair of electrons on nitrogen is potentially available for intermolecular bonding. The structural behaviour of Me_2NSiH_3 suggests that in silylamines there may be competition for the nitrogen lone pair of electrons between intramolecular $N \longrightarrow Si$ π bonding and intermolecular $N \cdots Si$ σ bonding.

Our previous *X*-ray studies [4-6] of silyl compounds have revealed several instances of crystals involving short contacts, or secondary bonding, between the $-SiH_3$ group in one molecule and a donor atom (such as N, O, or S) in an adjacent molecule. We have associated such interactions with changes in intramolecular geometry that are sometimes apparent when comparing crystal with gas-phase structures. Raman spectroscopic examinations of $^{14}N(SiH_3)_3$ and $^{15}N(SiH_3)_3$ in gas, liquid, and solid phases indicated planar heavy-atom skeletons in gaseous molecules but slight distortions from planarity in liquid and solid phases.[7] This structure analysis of trisilylamine was undertaken to determine the molecular geometry in the crystal, and to establish the extent of molecular association, if any.

Table 1. Atomic co-ordinates and thermal vibrational parameters † with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
N	0.506 5(8)	0.251 6(6)	0.514 2(8)
Si(1)	0.717 2(2)	0.267 4(2)	0.442 3(3)
Si(2)	0.220 4(2)	0.205 2(2)	0.304 2(3)
Si(3)	0.584 9(3)	0.285 0(2)	0.798 1(3)
H(11)	0.699(8)	0.383(6)	0.312(9)
H(12)	0.936(10)	0.318(7)	0.635(11)
H(13)	0.717(12)	0.124(9)	0.323(13)
H(21)	0.218(8)	0.181(5)	0.096(8)
H(22)	0.110(8)	0.067(6)	0.321(9)
H(23)	0.135(9)	0.323(6)	0.303(10)
H(31)	0.667(12)	0.143(8)	0.876(13)
H(32)	0.741(12)	0.442(9)	0.905(13)
H(33)	0.391(11)	0.256(7)	0.798(11)
	10^4U_{11}	10^4U_{22}	10^4U_{33}
N	214(25)	412(25)	211(25)
Si(1)	240(9)	384(9)	254(9)
Si(2)	221(9)	361(9)	236(9)
Si(3)	266(9)	392(9)	197(9)
	10^4U_{12}	10^4U_{13}	10^4U_{23}
N	22(18)	70(25)	59(20)
Si(1)	59(6)	129(8)	85(6)
Si(2)	50(6)	77(8)	58(6)
Si(3)	50(6)	104(8)	76(6)

	U/Å^2		U/Å^2
H(11)	0.018(13)	H(23)	0.022(13)
H(12)	0.035(16)	H(31)	0.054(20)
H(13)	0.059(12)	H(32)	0.069(24)
H(21)	0.007(11)	H(33)	0.041(17)
H(22)	0.019(13)		

† Anisotropic vibration: $t = \exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots 2hka^*b^*U_{12} + \cdots)]$; isotropic vibration: $t = \exp[-8\pi^2U\sin^2\theta/\lambda^2]$.

Experimental

Crystal Data.—$N(SiH_3)_3$, $M = 107.3$, m.p. = 167 K. At 115 K crystals are triclinic, $a = 6.84$, $b = 8.17$, $c = 6.87$ Å, $\alpha = 95.5$, $\beta = 119.1$, $\gamma = 98.6°$ (estimated standard deviations 0.3% assumed), $U = 325.3$ Å^3, $Z = 2$, $D_c = 1.10$ g cm^{-3}, Cu-K_α radiation (nickel filter), $\lambda = 1.5418$ Å, μ(Cu-K_α) = 57.2 cm^{-1}, space group $P\bar{1}$ (C_i^1, no. 2) by systematic absences and analysis.

The final least-squares weighting scheme was $w^{-1} = 1.00$ if $F_o < 7$ and $w^{-1} = 1 + 0.0040(F_o - 7)^2$ if $F_o > 7$, and the final value of an isotropic extinction coefficient was $g = 26(3) \times 10^{-6}$, where $F_c' = F_c[1 - (gF_c^2/\sin\theta)]$. A final difference-Fourier synthesis showed no peaks or troughs outside the range ± 0.3 e Å^{-3}. Final values of the discrepancy indices, over 651 reflections, were $R = \Sigma|\Delta|/\Sigma|F_o| = 0.051$ and $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.053$.

Procedure.—The compound is an air- and moisture-sensitive liquid at room temperature. Samples were sealed in thin-walled Pyrex glass capillaries and mounted on goniometer heads using heat-insulating Tufnol inserts. Single crystals were

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† *Supplementary data available* (No. SUP 23823, 6 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 2. Molecular geometry

(*a*) Interatomic distances (Å)

N-Si(1)	1.728(5)	Si(2)-H(21)	1.42(5)
N-Si(2)	1.727(5)	Si(2)-H(22)	1.31(5)
N-Si(3)	1.733(5)	Si(2)-H(23)	1.20(5)
Si(1)-H(11)	1.34(5)	Si(3)-H(31)	1.40(7)
Si(1)-H(12)	1.40(6)	Si(3)-H(32)	1.41(7)
Si(1)-H(13)	1.36(7)	Si(3)-H(33)	1.31(7)

(*b*) Angles (°)

Si(1)-N-Si(2)	120.1(3)	N-Si(1)-H mean	113(3)
Si(1)-N-Si(3)	119.5(3)	N-Si(2)-H mean	109(3)
Si(2)-N-Si(3)	120.4(3)	N-Si(3)-H mean	106(3)

(*c*) Distances (Å) of atoms from the least-squares best plane defined by N, Si(1), Si(2), Si(3)

N, −0.005(5); Si(1), 0.002(2); Si(2), 0.002(2); Si(3), 0.002(2); H(11), 1.05(5); H(12), 0.10(6); H(13), −1.08(8); H(21), −0.05(4); H(22), −1.05(5); H(23), 1.03(5); H(31), −1.28(7); H(32), 1.08(8); H(33), −0.08(6)

Table 3. Shortest intermolecular distances (Å) of each type

Shortest N · · · N	: N · · · N^{I}	4.08
	N · · · N^{II}	4.09
Shortest N · · · Si	: none within search distance of 4.2 Å	
Shortest N · · · H	: N · · · H(31^{I})	3.62
Shortest Si · · · Si	: Si(1) · · · Si(2^{III})	4.08
Shortest Si · · · H	: Si(3) · · · H(11^{IV})	3.21
	Si(2) · · · H(31^{I})	3.33
Shortest H · · · H	: H(23) · · · H(32^{II})	2.77
	H(13) · · · H(31^{I})	2.79

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I	$1 - x, -y, 1 - z$	III	$1 + x, y, z$
II	$1 - x, 1 - y, 1 - z$	IV	$x, y, 1 + z$.

grown *in situ* on a Nonius Weissenberg goniometer fitted with Nonius low-temperature nitrogen gas-stream equipment with some locally devised modifications. Intensity films were exposed using copper *X*-radiation and the multiple film-pack equi-inclination Weissenberg method. During photography a thin sheet of nickel foil was used as a diffracted beam filter (in addition to an incident beam Ni-filter) to reduce the background from *X*-ray fluorescence.

Initial attempts to record intensity data were unsuccessful. Although good single crystals were grown, the specimens suffered from radiation damage and were always destroyed within the time (*ca.* 10 h) required to record one layer of intensity data. Further samples of trisilylamine (that were thought to be significantly purer) yielded crystals that were more stable to *X*-radiation. Some darkening of these crystals occurred after prolonged irradiation but there was no discernable influence on the diffraction data. It is possible that the original crystals suffered damage as a result of a radiation-induced reaction with impurities.

Two different crystals were used for intensity data collection. Both crystals were grown from the same sample in the same capillary tube (diameter 0.4 mm). Crystal (1) was aligned along the *c* axis and used to record the Weissenberg levels *hk*0—4; crystal (2) was aligned along the *a* axis and used to record the levels 0—2*kl*. Cell parameters were determined from measurements of oscillation and zero-layer Weissenberg photographs and subsequently confirmed by reflection co-ordinates during microdensitometer scanning.

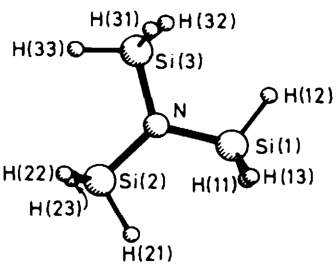

Figure 1. View of the $N(SiH_3)_3$ molecule showing the atomic labelling scheme

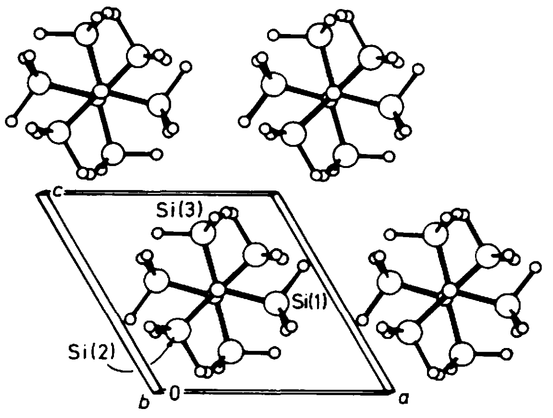

Figure 2. Unit cell and packing of $N(SiH_3)_3$ molecules

Integrated intensities were derived from the microdensitometer measurements performed by the S.E.R.C. Microdensitometer Service at Daresbury Laboratory, Warrington. In all, 1 008 reflections were measured in the hkl, $\bar{h}kl$, $h\bar{k}l$, $\bar{h}\bar{k}l$, $h\bar{k}\bar{l}$, and $hk\bar{l}$ regions of reciprocal space. These data were corrected for absorption effects using the SHELX program:[8] for each crystal enough faces were defined to approximate the required (cylindrical) shape and orientation. After further corrections for Lorentz and polarisation effects the data were scaled together and equivalent reflections merged (merging $R =$ 0.056). This process yielded 651 unique observed intensities (space group $P\bar{1}$ being assumed).

Structure Solution and Refinement.—The cell-parameter values and the approximate equivalence between the intensities of low order *hkl* with low order *lkh* reflections suggested a pseudo-hexagonal structure with molecules lying approximately in the *ac* plane at $y/b = \pm\frac{1}{4}$. Starting from the pseudo-hexagonal orientation, a planar heavy-atom model was adjusted by trial and error (and by reference to the rather ambiguous Patterson synthesis) until a satisfactory least-squares refinement was achieved. A subsequent difference-Fourier synthesis clearly revealed all nine hydrogen atoms. Weighted least-squares calculations to minimise the quantity $\Sigma w(|F_o| - |F_c|)^2$ were employed for final structure refinement. Hydrogen atoms were assigned isotropic vibration parameters; other atoms were assigned anisotropic parameters, and all the atomic parameters together with an isotropic extinction coefficient and overall scale factor were varied during the minimisation process. Throughout the structure analysis there was never any indication that the true space group was not $P\bar{1}$.

Atomic scattering factors for Si and N were taken from ref. 9 and for H from ref. 10. $\Delta f'$ and $\Delta f''$ corrections for Si and N atoms were from ref. 11. Calculations were performed using PRIME 550 and 750 computers of the Napier College computer unit and using programs written here, together with the SHELX program system.[8] Diagrams were prepared using computers of the Edinburgh Regional Computing Centre and using the PLUTO program system.[12]

Results

Final values of atomic parameters are given in Table 1, and details of intramolecular geometry and intermolecular contacts in Tables 2 and 3 respectively. Figures 1 and 2 illustrate aspects of the structure.

The cell parameters are subject to the usual errors associated with the Weissenberg film method. These errors are probably accentuated by the use of split-film cassettes for low-temperature work. Estimated standard deviations given in Tables 1—3 do not include contributions from errors in the cell parameters, but the e.s.d.s in the abstract do include such contributions.

Discussion

Planar molecules of trisilylamine pack in the crystal in a parallel fashion with the N atom of one molecule over the N atom of another. The N $\cdots$ N separation is 4.1 Å. There are no N $\cdots$ Si intermolecular interactions. The Si–N bond length in the crystal, mean 1.730(5) Å, does not differ significantly from the length determined by electron diffraction in the gas, 1.735(2) Å. With a planar heavy-atom skeleton the conformation of the $-SiH_3$ groups determines the overall molecular symmetry which (within experimental error) is precisely C_{3h} in the crystal. Here there is no ready comparison with the gas-phase structure: neither of the electron diffraction analyses [1] yielded reliable information about the hydrogen conformations.

In the crystal the heavy atoms vibrate so that their root-mean-square displacements in the direction parallel to the C_3 axis are some 30% greater than the displacements perpendicular to the axis. This thermal motion could be interpreted in several different ways leading to different conclusions about the equilibrium geometry of the heavy-atom skeleton. Three of the simpler interpretations, and their implications, are given below.

(*a*) The phases of vibration (of the three Si and one N atom) are random with respect to one another. This is the usual assumption in *X*-ray analysis. The heavy-atom geometry (as specified in Table 2) therefore refers to distances and angles between the time-averaged centres of gravity of electron distribution. No corrections for thermal motion can be evaluated.

(*b*) The heavy-atom vibrations parallel to the C_3 axis are all exactly in phase. This corresponds to a rigid-body vibration with the major vibration along the C_3 axis. In this case the distances and angles in Table 2 will be very close to the equilibrium bond lengths ($r_{eq.}$) and angles. No significant corrections to molecular geometry are expected: inspection of the thermal parameters suggests that rotary oscillations or screw displacements of the rigid body must be very small.

(*c*) The three Si atoms all vibrate exactly in phase while the N atom vibrates exactly out of phase. This would be dynamic inversion of a (slightly) pyramidal species. One feature which argues against this interpretation is that the centre of gravity of the molecule might be expected to remain fixed during inversion but this could not be so here. A fixed centre of gravity would require the r.m.s. displacement of N to be six times greater than the r.m.s. displacement of a Si atom, whereas the observed r.m.s. displacements are rather similar. If, despite the above, dynamic inversion was occurring, then corrections should be applied to the apparent molecular geometry to allow for the foreshortening effect on bond distances. Only a qualitative estimate of the correction is justified. [The method of data collection and the large *X*-ray absorption factors will have prevented the determination of accurate vibration parameters.] The estimated corrections imply a mean $r_{eq.}$(Si–N) length of *ca.* 1.738 Å with mean equilibrium Si–N–Si angle of *ca.* 119.0°.

One other aspect of the structure deserves comment. The crystal structure shows trisilylamine molecules stacked one above another with the nitrogen atom in one molecule more or less directly above the nitrogen in the molecule beneath. This arrangement implies an absence of polarity in the Si–N bonds, since if the Si–N bonds were polar nitrogen and silicon atoms would have opposite charges and the molecules would be unlikely to crystallise in a manner that places similar charges (on the N atoms) one above another. In turn this suggests that any intrinsic polarity in the Si–N σ bond must be offset by an equivalent and opposite ($p \longrightarrow d$) π interaction from N to Si.

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