Determination of the Molecular Structure of Tris(trimethylsilyl)amine in the Gas Phase by Electron Diffraction

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The structure and conformation of tris(trimethylsilyl)amine in the gas phase have been determined by electron diffraction. The three Si–N bonds are coplanar and 175.5(3) pm long (r_a). The trimethylsilyl groups are arranged so that the overall symmetry for the heavy atoms is very close to C_{3h}, with twists of just 5.2(24)° reducing the symmetry to C_3. The errors in parentheses are each one standard deviation, so this torsional distortion is barely significant. The trimethylsilyl groups had local C_s symmetry, with two NSiC angles of 111.5(7) and one of 112.6(4)°, and two CSiC angles 108.0(8)° and the other one thus 105.0°. Other major parameters are r(Si–C) 187.9(3) pm, r(C–H) 110.6(3) pm, and SiCH 110.1(4)°.

In structural studies of many silylamines, wide variations in angles SiNSi and SiNC have been observed, but Si–N distances have been remarkably constant. For example, the SiNSi angles in $NBu^t(SiH_3)_2$,[1] $NH(SiH_3)_2$,[2] and $NH(SiMe_3)_2$ [3] are 118.4(4), 127.7(1), and 131.3(15)°, while the lengths of the Si–N bonds are 173.5(1), 172.5(3), and 173.8(5) pm. In gaseous $NMe_2(SiH_3)$[4] the SiNC angles are 120.9(3)°, and change to 121.4(5) in $NMe_2(SiMe_3)$ in the gas phase and 122.9(1)° in the crystal.[5] Again, the Si–N bonds change little in length, from 171.3(5) pm in $NMe_2(SiH_3)$ to 171.0(5) and 171.9(1) pm in gaseous and crystalline $NMe_2(SiMe_3)$ respectively. Even in $NMe(SiMe_3)_2$, the most crowded silylamine studied so far,[6] the Si–N distance is only 171.9(4) pm. In all these compounds the sterically demanding groups are accommodated by changes of angles at nitrogen, adoption of conformations which minimise 1,3-interactions between methyl substituents on silicon, and to a lesser extent by compression of $SiMe_3$ groups, with reduction of the CSiC angles.

In the case of $N(SiMe_3)_3$ the SiNSi angles cannot exceed 120°. It is known that this compound, unlike other silylamines, cannot be prepared by direct reaction of a silyl halide with ammonia.[7] In that reaction only two silyl groups become bound to nitrogen, and this suggests that steric crowding is now significant. We therefore expect $N(SiMe_3)_3$, which is prepared *via* the alkali-metal salts $M^+[N(SiMe_3)_2]^-$, to show the effect of this crowding in lengthening of the Si–N bonds. In this paper we report the determination of the structure of $N(SiMe_3)_3$ in the gas phase, and show that the Si–N bonds are indeed unusually long for a silylamine.

Experimental

Tris(trimethylsilyl)amine was prepared from chlorotrimethylsilane and ammonia *via* the lithium bis(trimethylsilyl)amide salt.[7]

Electron diffraction data were recorded photographically using the Balzers' KDG-2 apparatus in Oslo[8] and Kodak Electron Image plates, with nozzle-to-plate distances of 498 and 248 mm, an accelerating voltage of 42 kV, and a nozzle temperature of 350 K. The electron wavelength (5.870 pm) was calibrated against the diffraction patterns of gaseous benzene [r_a(C–C) = 139.75 pm], and its estimated uncertainty is 0.1%.

Table 1. Camera distances, weighting functions, correlation parameters, and scale factors

Camera height/mm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor (k)
			nm^{-1}				
247.91	4	40	50	250	300	0.119	0.840(8)
497.84	2	16	50	120	150	0.485	0.833(10)

The optical densities of four plates from each of the two camera distances were recorded in a rectangular co-ordinate system using a Joyce–Loebl microdensitometer and the data were treated to give density values at even intervals of the scattering variable, s.[9] Further data reduction[10] was carried out in routine fashion using a blackness correction of $1.00 + 0.03D + 0.09D^2 + 0.03D.^3$ The uphill curve intensities $s^4I_{tot.}(s)$, in s intervals of 2 and 4 nm^{-1} for the long and short camera distances respectively, were transferred to Edinburgh, where least-squares refinements were carried out using established programs.[11] The data ranges and parameters used to define the off-diagonal weighting functions required in the refinements are given in Table 1, together with scale factors and correlation parameters. The complex scattering factors of Schäfer *et al.*[12] were used throughout the calculations.

Structural Analysis

Molecular Models.—In the earliest stages of the refinements of the structure of $N(SiMe_3)_3$ it was assumed that the three trimethylsilyl groups were identical, each having C_3 local symmetry, and with each methyl group having local C_{3v} symmetry. The torsion angles about the Si–N bonds could be constrained to be equal, giving C_3 symmetry to the molecule overall, or they could be refined independently. For each group the zero position was defined to be that in which one Si–C bond lay in a plane perpendicular to the molecular three-fold axis. Early refinements showed that the three Si–N bonds were coplanar within experimental error, and the data could be fitted well by a structure in which all three $SiMe_3$ groups had twist angles close to zero, at which position the overall symmetry was C_{3h}.

In these preliminary refinements each trimethylsilyl group

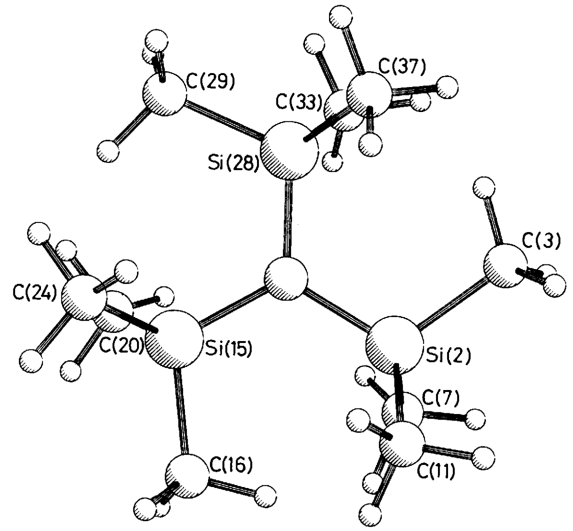

Figure 1. Perspective view of $N(SiMe_3)_3$ showing numbering of the heavy atoms

Table 2. Geometrical parameters (distances in pm, angles in °)

p_1	r(Si-N)	175.5(3)
p_2	r(Si-C)	187.9(3)
p_3	r(C-H)	110.6(3)
p_4	NSiC	112.6(4)
p_5	C*SiC*	105.0 (fixed[c])
p_6	C* tilt[a]	−3.3(14)
	NSiC*[b]	111.5(7)
	CSiC*[b]	108.0(8)
p_7	SiCH	110.1(4)
p_8	CH_3 torsion[a]	0.0 (fixed)
p_9	$SiMe_3$ torsion[a]	5.2(24)
	SiNSi	120.0 (fixed[c])

C Represents carbon atoms lying almost in the skeletal NSi_3 phase, and C* the out-of-plane carbon atoms. Errors in parentheses are estimated standard deviations obtained in the least-squares refinements.

[a] For definition, see text. [b] Dependent parameter. [c] Refined earlier, see text.

Table 3. Simplified valence force field for $N(SiMe_3)_3$[a]

k_r	SiN (3)[b]	3.10
	SiC (9)	2.85
	CH (27)	4.78
k_{rr}	SiN/SiC (3)	0.70
k_θ	HCH (27)	0.52
	SiCH (27)	0.40
	CSiC (9)	0.80
	NSiC (9)	0.40
	SiNSi (3)	1.10
k_τ	Si-N (3)	0.30
	Si-C (9)	0.10
k_γ	NSi_3 (1)	0.20

[a] See text for atomic co-ordinates and comments on vibrational frequencies. Stretch (k_r), stretch–stretch (k_{rr}) force constants in 100 aJ nm^{-2}; bend (k_θ), torsion (k_τ), and out-of-plane bend of a central atom of a four-atom group (k_γ) in aJ rad^{-2} (1 aJ = 1 mdyn Å). [b] The multiplicity of each force constant is given in parentheses.

was allowed freedom to tilt, so that its local three-fold axis no longer coincided with the Si–N bond. However, careful inspection of the planar C_{3h} model revealed that neither tilting of the $SiMe_3$ groups nor deviation from a planar NSi_3 skeleton serves the purpose of reducing steric strain, and in fact the refined tilt was insignificantly different from zero. In the final model of the molecule the presumption that each $SiMe_3$ group had local C_3 symmetry was abandoned, and Si–CH_3 groups which were almost in the NSi_3 plane were treated separately from the 'out-of-plane' methyl groups. The geometry of the molecule was then described by 12 parameters. Nine of these are listed in Table 2 for the final structure, which had C_3 symmetry and a planar NSi_3 skeleton. The remaining three parameters were two more $SiMe_3$ torsion angles, used when structures of lower symmetry were being investigated, and an angle used to define deviation of the skeleton from planarity. It was assumed that all the Si–CH_3 groups were identical and had C_{3v} local symmetry. The N–SiC_3 fragments were assumed to possess C_s symmetry, with the plane defined by nitrogen, silicon, and the 'in-plane' carbon atom [C(3): for atom numbering see Figure 1]. The angular positions of the methyl groups were then defined by the angles NSiC(3), C(7)SiC(11), and a tilt angle, between the bisectors of the preceding two angles. A positive angle represents movement of the two 'out-of-plane' methyl groups towards the centre of the molecule.

The conformations of the methyl groups were defined by a single torsion parameter. The zero positions were those in which one C–H bond of the 'in-plane' group eclipsed the Si–N bond, and for each 'out-of-plane' group one C–H bond eclipsed the other Si–C ('out-of-plane') bond. The three groups could then be rotated in a concerted fashion, each turning the same amount and in the same sense about its Si–C bond.

Calculated Amplitudes of Vibration.—Raman and i.r. spectra for $N(SiMe_3)_3$ have been recorded and assigned.[13] In order to obtain estimates of the many vibrational amplitudes which could not be determined from the electron diffraction data, a simplified valence force field was designed, roughly reproducing the observed frequencies. For this purpose overall C_{3h} symmetry was assumed, with C_{3v} local symmetry for $SiCH_3$ groups and $NSiC_3$ groups, and r(C–H) 110, r(Si–C) 188, r(Si–N) 175.5 pm, NSiC 112 and SiCH 110°. The force field is given in Table 3. Wavenumbers calculated with this field for the methyl groups were in the ranges 2 883, 2 995, and 2 997 cm^{-1} for stretches, 1 296—1 301 and 1 405 cm^{-1} for deformations, 805—824 and 758—770 cm^{-1} for rocks, and 231 cm^{-1} for torsions (nine modes in each frequency range). These are in fairly good agreement with their observed counterparts. The ν(Si–N) (calculated 928 and 442, observed 916 and 432 cm^{-1}) and ν(Si–C) [calculated 601—700 (six modes), observed 620—675 cm^{-1}] also fit well, but the 12 bending modes are difficult to assign. The calculated wavenumbers for these modes lie between 72 and 403 cm^{-1} and it seems probable that the observed set of frequencies is incomplete in this range. Moreover, the experimental data are said to be consistent with a pyramidal structure for the amine, rather than the C_{3h} symmetry applied in the calculations.

The amplitudes of vibration (u values) calculated from this approximate force field are similar to those reported for $N(SnMe_3)_3$.[14] The values obtained were subsequently used in the structural analysis to provide estimates of fixed vibrational parameters and reasonable relationships between those which were constrained at fixed ratios to one another. The force field was, however, considered to be too approximate to provide the information needed to make r_α refinements worthwhile, particular in view of the large number of low-frequency modes.

Refinement of Structure.—Most of the geometrical parameters defining the structure of $N(SiMe_3)_3$ could be refined without any difficulty, and require no comment, but particular reference must be made to the planarity or otherwise of the NSi_3 skeleton, the asymmetry of the $SiMe_3$ group, and the

Table 4. Interatomic distances and amplitudes of vibration (pm)

		Distance	Amplitude
r_1	Si–N	175.5(3)	6.2(2)
r_2	Si–C	187.9(3)	6.3 (tied to u_1)
r_3	C–H	110.6(3)	7.8(3)
r_4	N···C(3)	302.4(9)	13.2 (tied to u_8)
r_5	N···C(7)	300.3(13)	
r_6	C(3)···C(7)	303.9(15)	11.5 (tied to u_8)
r_7	C(7)···C(11)	298.1(4)	
r_8	Si···Si	304.0(5)	8.0(2)
r_9	Si(2)···C(29)	336.5(14)	12.2(12)
r_{10}	Si(2)···C(20)	363.5(27)	32.3(34)
r_{11}	Si(2)···C(24)	374.5(31)	
r_{12}	Si(2)···C(37)	433.0(21)	27.7(30)
r_{13}	Si(2)···C(33)	442.3(21)	
r_{14}	Si(2)···C(16)	467.2(9)	18.3(33)
r_{15}	C(3)···C(16)	523.1(19)	11.3(22)
r_{16}	C(11)···C(20)	529.9(28)	
r_{17}	C(7)···C(24)	550.8(20)	
r_{18}	C(3)···C(20)	319.3(29)	23.5 (tied to u_9)
r_{19}	C(3)···C(24)	356.7(36)	
r_{20}	C(7)···C(16)	581.1(16)	21.1(27)
r_{21}	C(11)···C(16)	583.1(16)	
r_{22}	C(7)···C(20)	460.9(19)	15.0 (fixed)
r_{23}	C(11)···C(24)	443.8(26)	
r_{24}	Si···H	248.7(6)	13.0(5)

Other long-range Si···H, N···H, C···H, and H···H distances were included in the refinements, but are not listed here.

Table 5. Least-squares correlation matrix × 100*

u_{10}	u_{12}	u_{14}	u_{15}	k_1	
51					p_4
	50	−75	58		p_6
	−57				p_9
				66	u_1
				51	u_8
			−58		u_{14}

* Only elements with absolute values ⩾50 are listed.

conformations of the $SiMe_3$ and CH_3 groups. When the SiNSi angle was allowed to vary, it refined to values in the range 118—120°, and it was strongly correlated with the $SiMe_3$ torsion angle. However, as the refinements progressed and the fit to the experimental data improved, the deviation from planarity became very small, and the SiNSi angle was eventually within 0.1 of 120°, with an estimated standard deviation (e.s.d.) of 0.1°. It was therefore decided that the planarity of the skeleton should be imposed, and the SiNSi angle was not included in subsequent refinements. However, at the very end the enforced planarity was relaxed. The SiNSi angle refined to 119.99°, and the e.s.d. of the $SiMe_3$ torsion angle increased from 2.4 to 2.6°.

Although the trimethylsilyl groups were allowed to have lower local symmetry than C_3, the deviation is not large. The angle between the two 'out-of-plane' Si–C bonds refined to *ca.* 105(2)° at an early stage, and later varied between 102 and 105°. The lower end of this range seems to be unrealistic, and so this angle was fixed for the final refinements. The other angles at silicon were free to refine, within the constraints of local C_s symmetry, but the two types of NSiC angle did not differ significantly from one another, at 111.5(7) and 112.6(4)°.

The conformation of the CH_3 groups was not well defined by the experimental data. Refinements were performed with the torsion angle set at values in the range 0 to 60°, and a slight preference was found for the eclipsed arrangement, which was assumed subsequently. The arrangement of the $SiMe_3$ groups was well determined, and from the earliest refinements onward it was clear that all three $SiMe_3$ torsion angles were close to zero. In these circumstances it was reasonable to assume that the three angles were identical, and refine a single parameter. Its final value, 5.2(24)°, is barely significantly different from zero, and as this is an r_a structure, the deviation from C_{3h} symmetry is almost certainly a shrinkage effect.

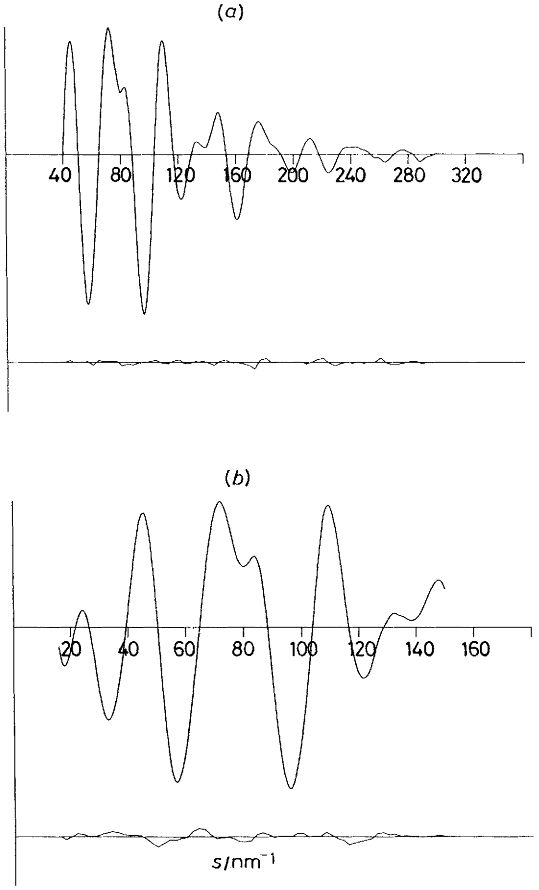

Figure 2. Observed and final weighted-difference molecular scattering intensity curves for $N(SiMe_3)_3$, recorded at camera distances of (*a*) 248 and (*b*) 498 mm

Finally, a careful check was made to see whether any other conformer could fit the experimental data. In particular, an arrangement similar to that reported[15] for the isoelectronic ion $[C(PMe_3)_3]^{2+}$ was investigated. None of these additional refinements was successful, and the lowest R factor (R_G) obtained was above 0.09, compared with 0.048 for the preferred C_{3h} arrangement.

The geometrical parameters obtained in the final refinement are listed in Table 2, and interatomic distances and amplitudes of vibration are given in Table 4. Table 5 includes the most significant elements of the final least-squares correlation matrix, and Figure 2 shows the molecular scattering intensity data. A perspective view of a molecule of $N(SiMe_3)_3$ and the radial distribution curve are depicted in Figures 1 and 3 respectively.

Discussion

The NSi_3 skeleton in $N(SiMe_3)_3$ is planar, as expected, both on steric grounds and by analogy with other trisilylamines, $N(SiH_3)_3$[16,17] and $N(SiH_2Me)_3$.[18] The bulky trimethylsilyl groups, which cannot separate from each other by increasing the SiNSi angle beyond 120°, are accommodated by elongation

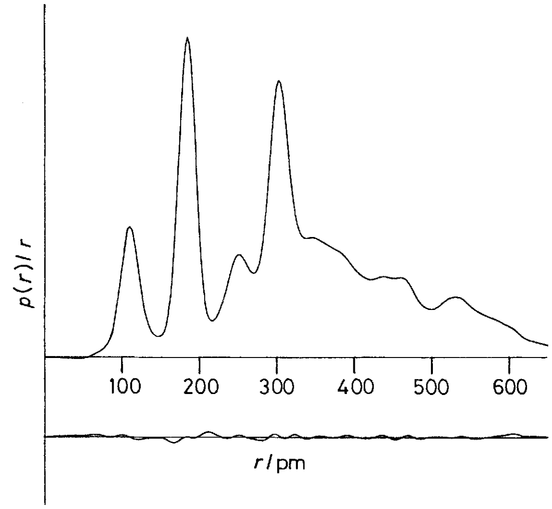

Figure 3. Observed and final weighted-difference radial distribution curves, $P(r)/r$, for $N(SiMe_3)_3$. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.000\,02\, s^2)/(Z_{Si} - f_{Si})(Z_N - f_N)$

of the Si–N bonds, to 175.5(3) pm, compared with 172.9(3) in $N(SiH_2Me)_3$[18] and 171.9(5) pm in $NMe(SiMe_3)_2$,[6] the most crowded silylamine studied previously in the gas phase. The longest Si–N distance in a simple silylamine is 173.8(5) pm, in $NH(SiMe_3)_2$.[3]

The Si–C bond length, at 187.9(3) pm, does not show any marked influence of the crowding, being only marginally longer than corresponding bonds in other trimethylsilylamines,[3,6] but there is some deviation from regular tetrahedral co-ordination at silicon, with the mean HSiC angle nearly 112°, compared with 107° for the CSiC angles. A similar effect was noted in $NMe(SiMe_3)_2$,[6] for which the mean HSiC angle was found to be 113.1(4)°, but in $NH(SiMe_3)_2$[3] the mean angle is only 110.7(5)°. Presumably in the latter case the crowding of the $SiMe_3$ groups is not so severe as in the N-methyl compound, and widening of the CNSi angle can reduce the strain. The distortion of the $SiMe_3$ groups from local C_3 symmetry is not very marked and is barely significant, and the apparent reduction of the angle between the two 'out-of-plane' Si–C bonds is not expected on steric grounds.

However, the overall conformation is exactly as expected. Any other arrangement of the $SiMe_3$ groups leads to much closer contacts between the various atoms, and it is quite clear that the observed arrangement is the only one that is feasible. When viewed along one of the Si $\cdots$ Si axes the six methyl groups bound to the two silicon atoms involved are in a perfectly staggered arrangement, so in this case the 1,3 interactions are minimised, as they are in other amines[3,19,20] and ethers[21,22] containing $SiMe_3$, $SiHMe_2$, or SiH_2Me groups.

Acknowledgements

We thank the British and Norwegian research councils (S.E.R.C. and N.A.V.F.) for financial support.

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Received 16*th January* 1989; *Paper* 9/00276F