Molecular Structure of Tris(methylsilyl)amine in the Gas Phase determined by Electron Diffraction

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The molecular structure of tris(methylsilyl)amine in the gas phase has been determined by electron diffraction. The NSi_3 skeleton is planar, and one Si–C bond lies perpendicular to this plane, while the other two Si–C bonds are twisted up to 20° out of the plane, so that the molecule overall approximates to C_s symmetry. Principal bond lengths (r_a) are: Si–N 172.9(3), Si–C 185.3(4), Si–H 149.2(10), and C–H 110.7(7) pm. The N–Si–C angle is 112.3(8)°.

THE planarity of the NSi_3 skeleton in trisilylamine was established 25 years ago,[1] and has been confirmed more recently,[2] and it has been shown that germanium-,[3] tin-,[4] and phosphorus-substituted [5] tertiary amines also have planar NM_3 skeletons. It is therefore remarkable that no structures of substituted trisilylamines in the gas phase have been reported, although many such amines are known. We have initiated a study of the electronic and steric effects of substituents at silicon on the structures of simple silyl compounds. In this paper we report the structure of tris(methylsilyl)amine, in which the main effect of methyl substitution has been to reduce the molecular symmetry, without greatly perturbing the geometry of the NSi_3 group.

EXPERIMENTAL

A sample of tris(methylsilyl)amine was prepared by the reaction of chloro(methyl)silane with ammonia,[6] and purified by fractional condensation *in vacuo*. Its purity was checked spectroscopically. Electron scattering patterns were recorded photographically on Kodak Electron Image plates using a Balzers' KD.G2 gas-diffraction apparatus,[7] with the sample held at 273 K and the nozzle at room temperature (*ca.* 295 K). Exposures were made with nozzle-to-plate distances of 250, 500, and 1 000 mm, giving data over a range of 10—304 nm^{-1} in the scattering variable, *s*. The data were obtained in digital form using a Joyce-Loebl automatic microdensitometer. The electron wavelength used, 5.661 ± 0.003 pm, was determined from the diffraction pattern of gaseous benzene.

All calculations were carried out on ICL 4-75 and 2970 computers using the programs for data reduction [8] and least-squares refinement [9] previously described. The weighting functions used to set up the off-diagonal weight matrices, and correlation parameters and scale factors, are given in Table 1. The complex scattering factors of Schäfer *et al.*[10] were used throughout the calculations.

STRUCTURE ANALYSIS

In the least-squares refinements, it was assumed that the geometries of the three $N–SiH_2CH_3$ fragments were identical, with local C_s symmetry for the $NSiH_2C$ groups and local C_{3v} symmetry for the $SiCH_3$ groups. The structure of each group was then defined by four bond lengths, the angles N–Si–C, H–Si–H, and Si–C–H, and the twist angle of the CH_3 group (defined to be zero when one C–H bond lies *trans* to the Si–N bond). In early refinements, the central NSi_3 skeleton was assumed to have C_{3v} symmetry, but the Si–N–Si angle consistently refined to 120°, and latterly the skeleton was assumed to have D_{3h} symmetry. As the conformation of the molecule as a whole does not have three-fold symmetry, it may be that there is some variation from

TABLE 1

Weighting functions, correlation parameters, and scale factors

Camera height mm	Scale factor	ΔS	$s_{\text{min.}}$	sw_1	sw_2	$s_{\text{max.}}$	Correlation parameter
		nm^{-1}					
250.1	0.615(16)	4	72	100	250	304	0.372
500.1	0.763(14)	2	34	45	135	154	0.469
999.8	0.661(16)	1	10	22.5	67.5	75	0.491

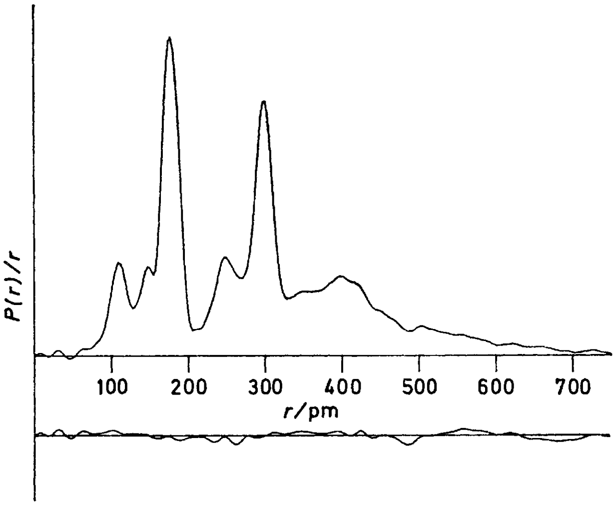

FIGURE 1 Radial distribution curve, $P(r)/r$, for $N(SiH_2CH_3)_3$. Before Fourier inversion the data were multiplied by $s\ \exp[-0.000\ 012\ s^2/(Z_{Si} - f_{Si})(Z_N - f_N)]$

TABLE 2

Molecular parameters for $N(SiH_2CH_3)_3$

(*a*) Independent geometrical parameters

		Distance, r_a/pm	Amplitude/pm
r_1	Si–N	172.9(3)	4.8(7)
r_2	Si–C	185.3(4)	
r_3	Si–H	149.2(10)	8.3(10)
r_4	C–H	110.7(7)	7.4(9)

		Angle/°
a_1	Si–N–Si	120.0 (fixed)
a_2	N–Si–C	112.3(8)
a_3	H–Si–H	109.0 (fixed)
a_4	Si–C–H	109.0(9)
a_5	CH_3 twist	60.0 (fixed) [a]
a_6	SiH_2Me twist 1 [a]	85.5(65)
a_7	SiH_2Me twist 2 [a]	−69.8(45)
a_8	SiH_2Me twist 3 [a]	180.0 (fixed)

(*b*) Dependent distances [b]

		Distance, r_a/pm	Amplitude/pm
d_5	Si ··· Si	299.5(6)	9.3(9)
d_6	Si ··· C	456.8(16)	28.2(71)
d_7	Si ··· C	460.1(11)	
d_8	Si ··· C	400.7(13)	18.7(37)
d_9	Si ··· C	400.7(13)	
d_{10}	Si ··· C	330.7(17)	37.3 (fixed)
d_{11}	Si ··· C	335.2(22)	
d_{12}	N ··· C	297.6(12)	8.1(36)
d_{13}	C ··· C	589.0(38)	33.3 (fixed)
d_{14}	C ··· C	411.0(66)	11.9(70)
d_{15}	C ··· C	434.6(53)	
d_{16}	Si ··· H	244.8(10)	10.7(10)

[a] See text. [b] Many Si ··· H, C ··· H, N ··· H, and H ··· H distances, which were included in the refinements, are not listed here. Errors (quoted in parentheses) are estimated standard deviations obtained in the least-squares analysis, increased to allow for systematic errors.

120° in the Si–N–Si angles, but such variation must be small, and has not been investigated.

The conformation of the methylsilyl groups was described by three twist angles, defined to be zero when the Si–C bonds lay perpendicular to the NSi_3 plane. A positive twist for the first SiH_2Me group moved its carbon atom away from the second SiH_2Me group. The three twist angles could be constrained to be equal, giving overall C_3 symmetry, or two could be constrained to be either equal, or equal and opposite. The latter constraint gave overall C_s symmetry if the third twist angle was zero or 180°.

The principal geometrical parameters, and many associated amplitudes of vibration, refined satisfactorily, as most of the one- and two-bond distances are represented by distinct peaks in the radial distribution curve (Figure 1). The CH_3 twist angle was found to be 60° (corresponding to an eclipsed conformation about the Si–C bond) by comparing *R* factors for refinements in which this angle was fixed at various values.

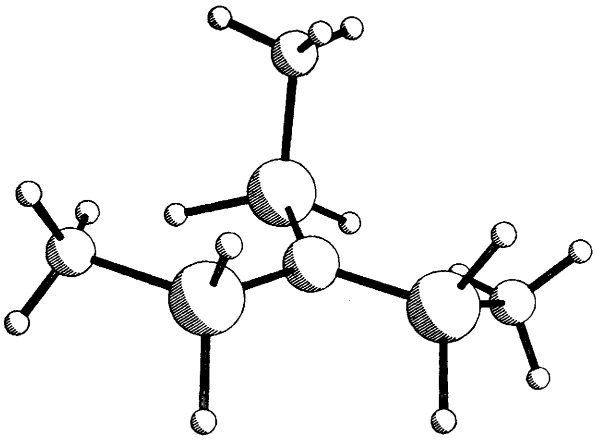

FIGURE 2 Perspective view of the molecule $N(SiH_2CH_3)_3$

Determination of the conformation adopted by the methylsilyl groups was dependent on analysis of the complex series of peaks above 330 pm in the radial distribution curve. Early refinements indicated that a reasonable fit (R_G = 0.13) could be obtained with a C_3 symmetry model, with the three twist angles close to 30°. However, subsequent work showed that a structure of C_s symmetry was also possible without unduly close contact between the methyl groups, and with this model the *R* factor was reduced to 0.10, with twist angles of 75, −75, and 180°. Finally, the requirement of strict C_s symmetry was relaxed, and the first two twist angles were allowed to refine, to 85 ± 6 and −70 ± 5°, with the *R* factor now 0.096. This final structure is depicted in Figure 2. It is not possible to be certain

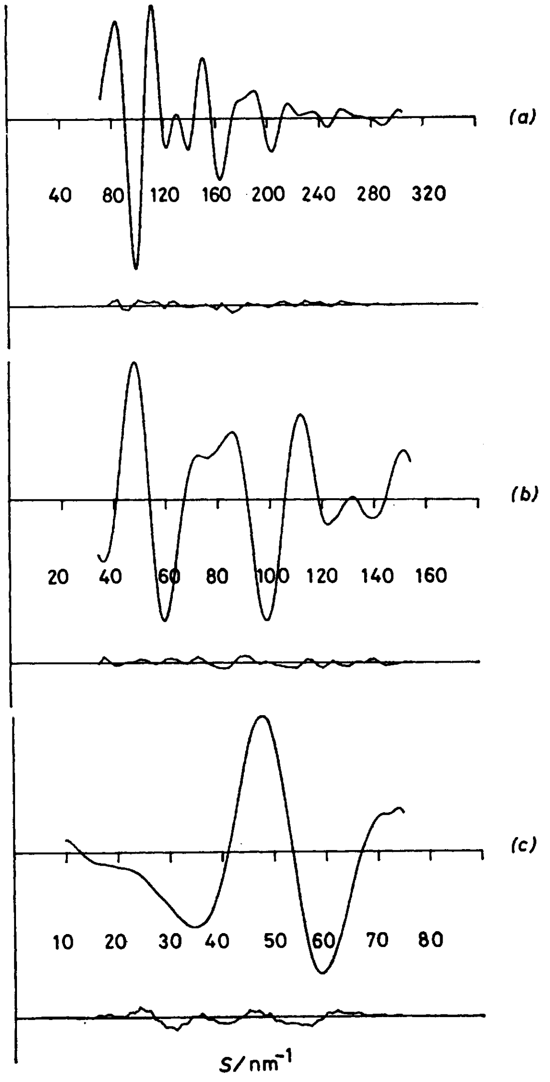

FIGURE 3 Experimental and final weighted difference molecular-scattering intensities for nozzle-to-plate distances of (*a*) 250, (*b*) 500, and (*c*) 1 000 mm

TABLE 3

Least-squares correlation matrix (× 100) for $N(SiH_2CH_3)_3$

	r_1	r_2	r_3	r_4	a_2	a_4	a_6	a_7	u_1	u_3	u_4	u_5	u_6	u_8	u_{12}	u_{14}	u_{16}	k_1	k_2	k_3
r_1	100				−78															
r_2		100	40						−72											
r_3			100						−43								−40		−59	−42
r_4				100		−52														
a_2					100															
a_4						100														
a_6							100						−47	81		−45				
a_7								100					65	−48						
u_1									100									58	58	
u_3										100										
u_4											100									
u_5												100			−92					
u_6													100			41				
u_8														100						
u_{12}															100					
u_{14}																100				
u_{16}																	100	40	42	
k_1																		100	62	
k_2																			100	46
k_3																				100

that no second conformer is present, nor that some other conformation with C_1 symmetry may not fit the data equally well, but all ranges of twist angles that seem physically reasonable have been explored, and the difference radial distribution curve shows no significant features above the noise.

The final parameters are listed in Table 2, and the least-squares correlation matrix is given in Table 3; the observed and final difference-intensity data are shown in Figure 3.

DISCUSSION

The most striking feature of the structure of tris(methylsilyl)amine is that the NSi_3 skeleton is very similar to that of trisilylamine, despite the potential distorting effects of the methyl substituents. The skeleton is completely planar, and the Si–N distance [172.9(3) pm] is only marginally less than that in unsubstituted trisilylamine [173.4(2) pm].[2]

The Si–C distance, 185.3(4) pm, is significantly less than that in methylsilane (186.7 pm),[11] but greater than that in fluoro(methyl)silane (184.8 pm).[12] The differences may be attributed to the effects of the electronegative substituents in the amine and fluorosilane.

The conformation adopted is of interest, in that the three-fold symmetry is not retained, unlike in the case of tris(difluorophosphino)amine.[5] In all probability the average structure has C_s symmetry, and the slight apparent distortion from this is a shrinkage effect caused by a torsional vibration. In some respects, the conformation resembles that adopted by $N(SCF_3)_3$,[13] which also has C_s symmetry, although in that case all the S–C bonds lie perpendicular to the skeletal plane, whereas in the present compound two of the Si–C bonds are not far from lying in the skeletal plane. We intend to study the conformations of other mono(methylsilyl) compounds, to see if there are any general principles that determine the favoured forms.

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REFERENCES

[1] K. Hedberg, *J. Am. Chem. Soc.*, 1955, **77**, 6491.
[2] B. Beagley and A. R. Conrad, *Trans. Faraday Soc.*, 1970, 2740.
[3] C. Glidewell, D. W. H. Rankin, and A. G. Robiette, *J. Chem. Soc. A*, 1970, 2935.
[4] L. S. Khaikin, A. V. Belyukov, G. S. Koptev, A. V. Golubinskii, and L. V. Vilkov, *J. Mol. Struct.*, 1980, **66**, 191.
[5] D. E. J. Arnold, D. W. H. Rankin, M. R. Todd, and R. Seip, *J. Chem. Soc., Dalton Trans.*, 1979, 1290.
[6] E. A. V. Ebsworth and H. J. Emeléus, *J. Chem. Soc.*, 1958, 2150.
[7] B. Beagley, A. H. Clark, and T. G. Hewitt, *J. Chem. Soc. A*, 1968, 658.
[8] D. M. Bridges, G. C. Holywell, D. W. H. Rankin, and J. M. Freeman, *J. Organomet. Chem.*, 1971, **32**, 87.
[9] A. S. F. Boyd, G. S. Laurenson, and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **71**, 217.
[10] L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, 1971, **55**, 3055.
[11] R. W. Kilb and L. Pierce, *J. Chem. Phys.*, 1957, **27**, 108.
[12] L. Pierce, *J. Chem. Phys.*, 1958, **29**, 383.
[13] C. J. Marsden and L. S. Bartell, *J. Chem. Soc., Dalton Trans.*, 1977, 1582.