Electron Diffraction Study of the Molecular Structure of *N*-Methylbis(trimethylsilyl)amine in the Gas Phase

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The molecular structure of $NMe(SiMe_3)_2$ in the gas phase has been determined by electron diffraction. The molecule has a planar $NCSi_2$ skeleton with the SiNSi angle 129.4(6)°. Other important parameters (r_a) are: r(Si–N) 171.9(4), r(Si–C) 187.5(3), r(C–N) 149.8(7) pm; angle CSiC 105.6(4)°. The steric requirements of the bulky $SiMe_3$ groups are accommodated by the wide SiNSi and narrow CSiC angles, rather than by elongation of the Si–N bonds. The heavy-atom skeleton has C_2 symmetry, with the $SiMe_3$ groups twisted 35.2(5)° away from the positions in which one Si–C bond on each group eclipses the N–C bond, and this has the effect of minimising interactions between methyl groups on silicon and on nitrogen.

Extensive studies of silylamines and their derivatives have shown that, in general, trisilylamines[1,2] and disilylamino compounds[3–7] have planar co-ordination at nitrogen, but dialkyl(silyl)amines[8] have shallow pyramidal geometry. One exception to this generalisation is $NMe_2(SiMe_3)$,[9] which has a planar NC_2Si skeleton in the gas phase, and is only very slightly distorted from planarity in the crystalline phase. It is possible that in this case the bulk of the trimethylsilyl group prevents substantial distortion from the planar structure, although we cannot tell whether the observed structures of dimethyl(silyl)-amines represent potential minima, or whether there are large shrinkage effects arising from large amplitude out-of-plane deformation vibrations.

In the silylamines studied so far, the effects of increasing the number of methyl substituents are small, and apart from the planarity or near planarity of the skeleton of $NMe_2(SiMe_3)$ the most interesting features are some systematic trends, which are presumably electronic in origin, and the conformations. Interactions between methyl groups on two silicon atoms separated by two bonds seem to be more important than those between methyl groups on adjacent silicon and nitrogen atoms. The Si–C bonds always adopt staggered positions when viewed along the Si···Si axes, and this is particularly important in compounds containing trimethylsilyl groups, such as $NH(SiMe_3)_2$.[5] In this compound the bulky $SiMe_3$ groups can avoid each other by widening the central SiNSi angle, and in this paper we present results for $NMe(SiMe_3)_2$, which behaves in much the same way. Consequently, even with seven methyl groups, there are no signs of major lengthening of bonds or angular distortions other than some compression of the CSiC angles, and $N(SiMe_3)_3$ is therefore unique among the methyl-substituted silylamines in showing substantial evidence of steric strain.[10]

Experimental

Electron diffraction scattering intensities for a sample of *N*-methylbis(trimethylsilyl)amine (Aldrich) were recorded on Kodak Electron Image photographic plates using the Edinburgh gas diffraction apparatus[11] operating at *ca.* 44 kV. The sample and nozzle were kept at room temperature during the experiments. Scattering patterns for benzene were also recorded, so that the electron wavelength and nozzle-to-plate distances could be calibrated. Data from three plates at the long camera distance and two at the short distance were obtained in digital form using a Joyce-Loebl MDM6 microdensitometer at the S.E.R.C. Daresbury Laboratory.[12] In subsequent analysis of the data established data-reduction[12] and least-squares refinement programs[13] and the scattering factors of Schäfer *et al.*[14] were used. The weighting points used in setting up the off-diagonal weight matrix, *s* ranges, scale factors, correlation parameters, and electron wavelengths are all given in Table 1.

Table 1. Weighting functions, correlation parameters, and scale factors for $NMe(SiMe_3)_2$

Camera height/ mm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor	Electron wavelength/ pm
	nm^{-1}							
128.4	4	60	80	300	340	−0.169	0.741(9)	5.707
285.5	2	20	40	124	144	0.442	0.698(4)	5.708

Structure Refinement.—For the purposes of the least-squares refinements it was assumed that the Me groups had local C_{3v} symmetry and that the $SiMe_3$ groups had C_3 symmetry. The structure of the $SiMe_3$ group was then defined by the Si–C and C–H bond lengths, the angles CSiC and SiCH, and a methyl twist angle, which was taken to be positive for a clockwise rotation from the staggered position, viewed from C to Si. The local C_3 axes of the $SiMe_3$ groups were allowed to deviate from the lines of the Si–N bonds, in the SiNSi plane, and a positive tilt represented movement of the groups away from each other. The $SiMe_3$ groups were also allowed to twist about the Si–N bonds, with a positive twist clockwise when viewed from Si to N, and with the zero position defined so that one Si–C bond of the group lay *anti* with respect to the further N–Si bond. The twist angles for the two groups, φ_1 and φ_2, could be constrained to be equal, giving C_2 symmetry for the $N(SiC_3)_2$ skeleton, to be equal and opposite (C_s symmetry), or to be related by $\varphi_1 + \varphi_2 = 180°$, which allowed investigation of structures with the $SiMe_3$ groups intermeshing as in a pair of cogwheels. The Si–N distance and SiNSi angle completed the parameter list for the $N(SiMe_3)_2$ fragment, and the N-methyl group was described by C–N and C–H bond lengths (the latter assumed to be the same as in the Si-methyl groups), the NCH angle, a twist angle, defined to be zero when one C–H bond lay in a plane perpendicular to the SiNSi plane, and an angle representing the deviation of the NCSi skeleton from planarity, defined as the angle between the N–C bond and the SiNSi plane.

This last angle was shown in early tests to be zero or very nearly so, and planarity of the skeleton was therefore assumed until the final stages of the refinement. The radial distribution curve (Figure 1) shows a clear C–H peak, and a shoulder attributable to the C–N distance on the side of the biggest peak, which is due to the Si–C and Si–N bonded pairs of atoms. All

Table 2. Molecular parameters

r(C-N)/pm	149.8(7)
r(Si-N)/pm	171.9(4)
r(Si-C)/pm	187.5(3)
r(C-H)/pm	110.8(3)
SiNSi/°	129.4(6)
CSiC/°	105.6(4)
SiCH/°	110.3(3)
NCH/°	111 (fixed)
$SiMe_3$ twist/°	35.2(5)
$SiMe_3$ tilt/°	3.7(6)
$SiCH_3$ twist/°	0 (fixed)
NCH_3 twist/°	20 (fixed)
Deviation from planarity	0 (see text)

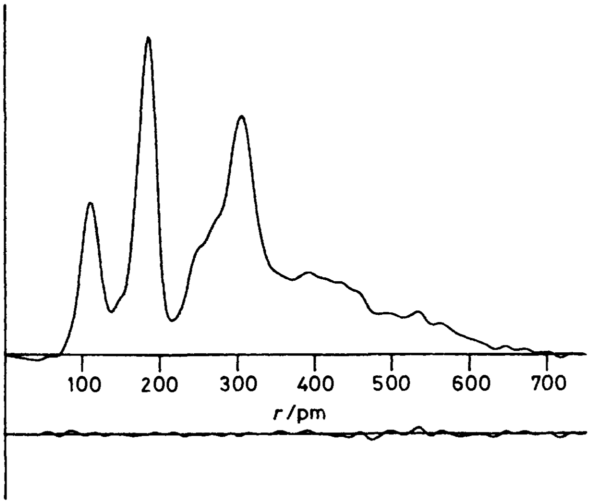

Figure 1. Observed and final difference radial distribution curves, $P(r)/r$, for $NMe(SiMe_3)_2$. Before Fourier inversion the data were multiplied by $s\cdot\exp[-0.000\,02s^2/(Z_{Si}-f_{Si})(Z_N-f_N)]$

four bonded distances and their associated amplitudes of vibration refined satisfactorily, as did the three principal valence angles, SiNSi, CSiC, and SiCH. The two-bond distances associated with these angles are Si(N)Si and Si(N)C, C(Si)C and N(Si)C, and Si(C)H, which contribute to the peak and shoulders visible in the radial distribution curve between *ca.* 250 and 310 pm. Four amplitudes of vibration for distances in this region were refined.

The outer part of the radial distribution curve is much more complicated, and decays fairly uniformly from 300 to 700 pm, with relatively small undulations. It is tempting to identify particular features with particular pairs of atoms, but much more important is the fit of the large number of different atom pairs separated by three or more bonds to the whole envelope. The parameters of greatest significance in achieving a satisfactory fit were the twist angles for the two $SiMe_3$ groups. Tests using the C_2, C_s, and cogwheel models showed that twist angles near 30° for the C_2 and cogwheel models (which are identical at 30°) were most promising, and the best fit was eventually obtained with the C_2 model and an angle of 35°. When the two angles were allowed to move independently they refined to 34 ± 5 and 35 ± 6°, so thereafter the C_2 constraint was applied.

The tilt of the $SiMe_3$ groups refined easily, to give a reasonable value of 3.7(6)°, but the remaining parameters (angle NCH, and twist angles for Si-methyl and N-methyl groups) were not well determined. Optimum values were found by varying these parameters stepwise, and they were then fixed.

Table 3. Interatomic distances (r/pm) and amplitudes of vibration

	Distance	Amplitude
C-N	149.8(7)	5.3(6)
Si-N	171.9(4)	5.9(2)
Si-C	187.5(3)	6.0(1)
C-H	110.8(3)	8.3(2)
Si(C)H	248.7(7)	11.5(3)
N(Si)C	294.7(17)	11.0(4)
	299.4(11)	
	305.8(10)	
C(Si)C	298.7(12)	
Si(N)Si	310.8(12)	9.5(5)
Si(N)C	272.1(8)	7.5(4)
N(C)H	215.9(7)	12.0 (fixed)
Si(NSi)C	372.3(15)	35.0 (refined, then fixed)
	421.8(14)	
	454.5(19)	

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

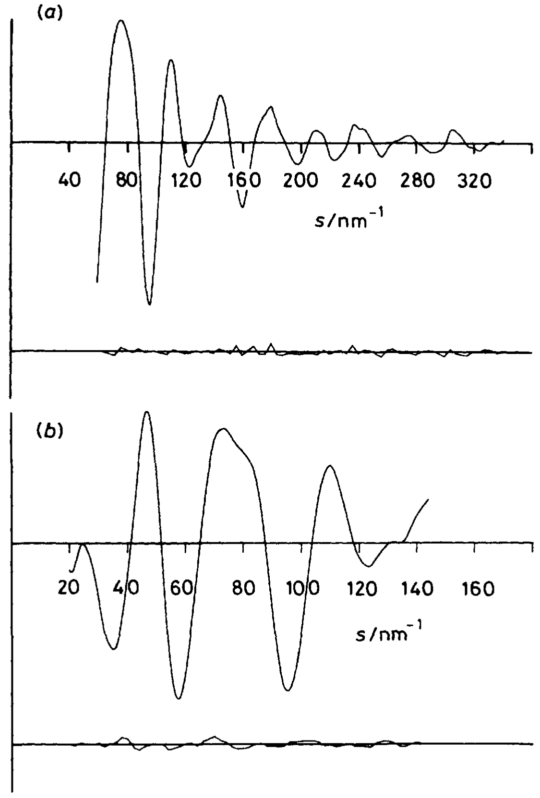

Figure 2. Observed and final weighted difference molecular scattering intensity curves for $NMe(SiMe_3)_2$, recorded at nozzle-to-plate distances of (*a*) 128 and (*b*) 286 nm

Finally, the test on the planarity of the $NCSi_2$ skeleton was repeated. The best fit to the data was for a structure which was very close indeed to being planar, but dip angles of up to 10°, corresponding to sums of angles at nitrogen down to 359°, cannot be ruled out.

The parameters obtained in the final refinement, for which the R factor, R_G, was 0.057, are given in Table 2, and interatomic distances and amplitudes of vibration are listed in Table 3. Table 4 gives the most significant elements of the least-squares correlation matrix. Note that the errors quoted in Tables 2 and

Table 4. Least-squares correlation matrix (× 100)*

SiNSi	Tilt angle	u(Si–N)	u[N(Si)C]	u[Si(N)C]	u[C(SiC)H]	Scale factor 1	
58			−64				r(C–N)
			−69			−50	r(Si–N)
	−54		−54		69		SiNSi
	52						CSiC
		74				66	u(Si–C)
						54	u(C–H)
				53			u[Si(C)H]

* Only elements with absolute values ≥50% are included.

Table 5. Molecular parameters: distances (pm) and angles (°) for some disilylamines

Compound	r(Si–N)	r(Si–C)	r(C–N)	SiNSi	SiNC	NSiC	CSiC	Ref.
$NH(SiH_3)_2$	172.5(3)			127.7(1)				3
$NMe(SiH_3)_2$	172.6(3)		146.5(5)	125.4(4)	117.3(2)			7
$NMe(SiH_2Me)_2$	171.8(3)	186.4(5)	149.2(12)	125.6(10)	117.2(5)	113.5(18)		6
$NH(SiHMe_2)_2$	172.7(3)	186.7(3)		130.4(15)		110.2(3)	112.8(11)	4
$NMe(SiHMe_2)_2$	172.7(4)	187.2(3)	148.3(7)	126.1(5)	116.9(3)	110.8(5)	115.5(10)	6
$NH(SiMe_3)_2$	173.8(5)	187.6(1)		131.3(15)		110.7(5)*	108.2(5)	5
$NMe(SiMe_3)_2$	171.9(4)	187.5(3)	149.8(7)	129.4(6)	115.3(3)	113.1(4)*	105.6(4)	This work

* Mean value: the NSiC angles are not equal, because the $SiMe_3$ groups are tilted away from each other.

3 are estimated standard deviations obtained in the least-squares analysis, increased to allow for systematic errors. The molecular scattering intensities and difference curves are shown in Figure 2.

Discussion

Structural data are now available for all the methyl derivatives of disilylamine that have so far been prepared, and important parameters are listed in Table 5. There is remarkably little variation in the Si–N and Si–C bond lengths, and the rather short Si–N distance found in the present study makes it clear that there is no systematic lengthening as the number of methyl substituents on silicon increases. The mean Si–N distance in these disilylamines is 172.6 pm, compared with 171.4 pm in four monosilylamines,[8,9] and around 174 pm in three trisilylamines.[1,2,10] The C–N bonds are consistently long, averaging 148.5 pm in the methyl(disilyl)amines, compared with 145.9 pm in the dimethyl(silyl)amines.[8,9]

All the compounds in Table 5 have planar skeletons, although the positions of the amino hydrogen atoms are unknown or poorly determined, and all have wide SiNSi angles. The presence of an N-methyl group reduces the SiNSi angle by 2—4°, while methyl substituents on silicon widen this angle slightly. Angles between Si–N and Si–C bonds at silicon are variable, but this is to be expected, as frequencies for deformation modes involving these bonds are often 200 cm^{-1} or less, and the force constants are correspondingly small. As the $SiMe_3$ groups are tilted away from each other by 3.7° in $NMe(SiMe_3)_2$, the NSiC angles are not equal: the individual angles are 110.1, 112.8, and 116.5°.

In $NMe(SiMe_3)_2$ the methyl groups are accommodated by the wide SiNSi angle, compression of the $SiMe_3$ groups by narrowing the CSiC angles, and tilting of these groups away from each other, but above all by the adoption of a conformation which minimises contacts between methyl groups, including both those on silicon and the unique N-methyl group. The view of the molecule along the Si $\cdots$ Si axis (Figure 3) shows this clearly. As in other compounds containing $-SiMe_3$,[5,15] $-SiHMe_2$,[4,6,16] or $-SiH_2Me$[6,16] groups, the 1,3-interactions between methyl substituents on the two silicon atoms seem to be important, and so there is an almost staggered arrangement of the two $SiMe_3$ groups when viewed along this axis. The interactions with the N-methyl group are then minimised by the adoption of a conformation with C_2 symmetry, and two equal CNSiC dihedral angles of 35°. These N-methyl–Si-methyl interactions are further reduced by the tilting of the $SiMe_3$ groups. The shortest H $\cdots$ H distances in our final model are close to 200 pm for both $SiMe_3 \cdots SiMe_3$ and $SiMe_3 \cdots NMe$ interactions, and this distance is considerably less than twice the van der Waals radius of hydrogen, but no account can be taken of possible distortions or displacements of individual methyl groups. The true H $\cdots$ H distances are probably much greater than this, but what is clear is that the two different types of interactions between methyl groups are of roughly equal importance.

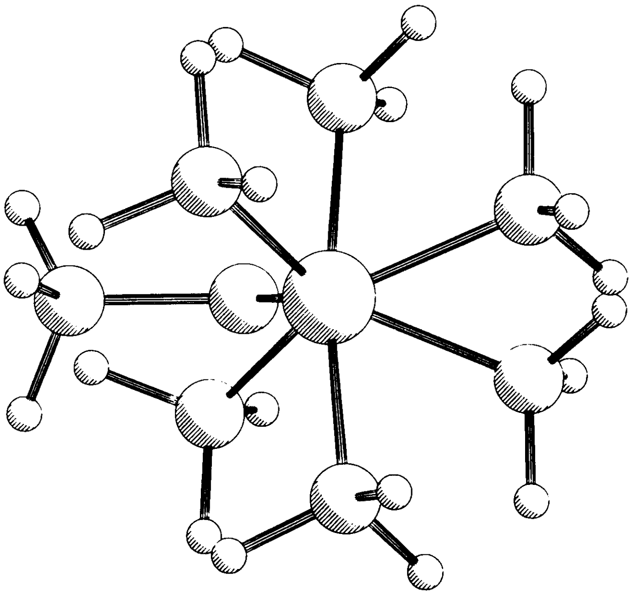

Figure 3. View of a molecule of $NMe(SiMe_3)_2$, projected along the Si $\cdots$ Si axis

Acknowledgements

We thank the S.E.R.C. for financial support and for use of the microdensitometer service.

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Received 26*th June* 1986; *Paper* 6/1293