N,N-Dimethyl(trimethylsilyl)amine: Crystal and Molecular Structure at 116 K and Gas Phase Structure by Electron Diffraction†

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The structure of $NMe_2(SiMe_3)$ has been studied in the crystalline phase at 116 K by *X*-ray crystallography and in the gas phase at 295 K by electron diffraction. The solid phase structure consists of essentially isolated molecules with a Si–N bond length of 1.719 4(12) Å. The geometry at silicon is nearly tetrahedral and that at nitrogen is slightly non-planar, with angles CNC 111.95(12), SiNC 122.92(10) and 122.91(10)°. The molecule possesses non-crystallographic C_s symmetry and the N-bonded methyl groups are distorted from planarity towards the unique Si-bonded methyl group, which is bent back to give an NSiC angle of 113.93(6)°. The conformation of the Si-methyl groups is such that one CH vector of each is approximately parallel to the NSi direction; for those bonded to nitrogen, one CH bond of each lies close to the CSiN plane. In the vapour the $SiNC_2$ skeleton was found to be planar. Principal parameters (r_a) are: *r*(Si–N) 1.710(5), *r*(Si–C) 1.868(4), *r*(C–N) 1.462(4) Å; angles SiNC 121.4(5), NSiC 110.3(7), CNC 117.1(10)°. The molecule is distorted from C_s symmetry by a 9.6(20)° twist of the $SiMe_3$ group and by twists of −12.1(45)° for each of the methyl groups on silicon.

It has long been known that trimethylamine, in common with other trialkylamines, has a pyramidal structure in the gas phase,[1] whereas trisilylamines have planar NSi_3 skeletons.[2] When nitrogen is bonded to both silyl and methyl groups the combination of two silyl and one methyl substituent appears to confer planarity at nitrogen on the structure.[3,4] One silyl and two methyl groups, on the other hand, results in shallow pyramidal geometry at nitrogen for those amines whose structures have been studied, *viz.* $NMe_2(SiH_3)$, $NMe_2(SiH_2Me)$ and $NMe_2(SiHMe_2)$.[5] For these compounds, however, it is not possible to be certain that the average structure is truly pyramidal or whether the geometry at nitrogen is, in fact, planar with a large amplitude out-of-plane vibration. It is thus of interest to look at the crystal structures of these amines with the proviso that 'floppy' molecules could have phase-dependent structures. Unfortunately $NMe_2(SiH_3)$ forms a cyclic pentamer in the crystal,[6,7] which although an interesting and important result, sheds no light on the problem. It proved impossible to grow crystals of $NMe_2(SiH_2Me)$ and $NMe_2(SiHMe_2)$ as both compounds form glasses on cooling. We are therefore left with $NMe_2(SiMe_3)$ as the last member of the series. Neither the gas- nor the solid-phase structure of this amine had been reported and we embarked on the present studies with a view to elucidating this structural puzzle.

Experimental

A sample of $NMe_2(SiMe_3)$ was prepared by the gas phase reaction of $SiMe_3Cl$ and $NHMe_2$. The product was separated and purified by fractional condensation *in vacuo* and its purity verified by i.r. and n.m.r. spectroscopy.

Crystallography.—A sample of $NMe_2(SiMe_3)$, sealed in a 0.4-mm diameter Pyrex capillary tube glued to a metal mount, was secured in a goniometer head. A single crystal was grown, and its quality and singularity checked, on an Enraf-Nonius Weissenberg goniometer equipped with a ULT-1 nitrogen-stream cooling device. For data collection the same crystal was transferred without melting (as described previously[8]) to an Enraf-Nonius CAD4 diffractometer equipped with a similar low-temperature system.

Crystal data. $C_5H_{15}NSi$, $M = 117.27$, triclinic, $a = 6.458\,1(13)$, $b = 7.331\,6(21)$, $c = 9.5470(22)$ Å, $\alpha = 85.087(9)$, $\beta = 77.990(4)$, $\gamma = 63.877(5)$°, $U = 397.1(13)$ Å^3, $T = 116$ K, space group $P\bar{1}$ (from E-statistics and successful refinement), D_m not determined, $Z = 2$, $D_c = 0.981$ g cm^{-3}. Sample: colourless, cylindrical crystal 0.4 × 0.4 × 0.5 mm, $F(000) = 132$, $\mu(\text{Mo-}K_\alpha) = 1.94$ cm^{-1}.

Data collection and processing.[8] CAD4 diffractometer, $\omega/2\theta$ mode with ω-scan width = $0.85 + 0.35 \tan \theta$, $T = 116$ K, graphite-monochromated Mo-K_α radiation; 2 502 reflections measured ($1 \leqslant \theta \leqslant 30°$, $+h \pm k \pm l$), 2 312 unique, giving 2 084 with $F > 2\sigma(F)$, no decay correction necessary, no absorption correction applied.

Structure solution and refinement. Patterson (Si) and an iterative combination of full-matrix least-squares refinement and difference Fourier syntheses located all atoms. Full-matrix least-squares refinement (on *F*) was carried out, with all non-H atoms anisotropic, H atoms isotropic. The weighting scheme $w^{-1} = [\sigma^2(F_o) + 0.004\,514\,F_o^2]$ gave satisfactory agreement analysis; final $R = 0.0447$, $R' = 0.0628$. Maximum and minimum residues in ultimate ΔF synthesis were 0.62 and −0.79 e Å^{-3} respectively; $S = 1.138$. Programs, computers, and sources of scattering factors used are given in ref. 8. Table 1 lists derived fractional co-ordinates and Table 2 lists interatomic distances and interbond angles.

Electron Diffraction.—Kodak Electron Image plates were used to record electron diffraction scattering intensities, obtained using the Edinburgh diffraction apparatus[9] with nozzle-to-plate distances of 128 and 286 mm and an accelerating voltage of *ca.* 44 kV. The sample and nozzle were maintained at room temperature (295 K) throughout the experiment. Data were obtained in digital form using a computer-controlled

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† *Supplementary data available* (No. SUP 56368, 6 pp.): thermal parameters, torsion angles, atomic orbital parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Fractional atomic co-ordinates with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Si(1)	0.219 15(5)	0.384 82(4)	0.248 19(3)	H(22)	0.577(4)	0.290(3)	0.096 0(22)
N(1)	0.127 09(18)	0.640 60(15)	0.271 99(12)	H(23)	0.401(4)	0.340(3)	−0.001 9(23)
C(1)	−0.039 02(25)	0.344 94(22)	0.228 74(18)	H(31)	0.372(3)	0.111(3)	0.395 1(21)
C(2)	0.453 69(24)	0.274 79(20)	0.086 49(14)	H(32)	0.215(4)	0.295(3)	0.497 9(23)
C(3)	0.335 44(24)	0.247 29(20)	0.407 87(14)	H(33)	0.471(4)	0.264(3)	0.421(3)
C(4)	0.254 7(3)	0.720 99(22)	0.335 65(17)	H(41)	0.376(4)	0.606(3)	0.390(3)
C(5)	−0.041 31(25)	0.795 01(20)	0.195 77(16)	H(42)	0.144(4)	0.826(4)	0.400 4(25)
H(11)	0.010(4)	0.192(4)	0.227(3)	H(43)	0.340(4)	0.789(3)	0.262 8(21)
H(12)	−0.089(5)	0.398(4)	0.143(3)	H(51)	−0.128(4)	0.747(3)	0.151 7(23)
H(13)	−0.171(5)	0.405(4)	0.316(3)	H(52)	0.033(4)	0.857(3)	0.108 8(23)
H(21)	0.503(4)	0.132(4)	0.075 3(24)	H(53)	−0.152(4)	0.910(3)	0.272 3(22)

Table 2. Intramolecular geometry

Interatomic distances (Å)

Si(1)–N(1)	1.719 4(12)	C(1)–H(11)	1.02(3)	C(2)–H(23)	0.982(23)	C(4)–H(42)	0.95(3)
Si(1)–C(1)	1.862 2(17)	C(1)–H(12)	0.93(3)	C(3)–H(31)	0.936(21)	C(4)–H(43)	1.032(23)
Si(1)–C(2)	1.869 1(15)	C(1)–H(13)	1.02(3)	C(3)–H(32)	1.001(23)	C(5)–H(51)	0.957(23)
Si(1)–C(3)	1.858 0(15)	C(2)–H(21)	0.960(25)	C(3)–H(33)	0.97(3)	C(5)–H(52)	1.042(24)
N(1)–C(4)	1.447 1(20)	C(2)–H(22)	0.875(24)	C(4)–H(41)	1.052(25)	C(5)–H(53)	1.056(22)
N(1)–C(5)	1.448 5(19)						

Interbond angles (°)

N(1)–Si(1)–C(1)	108.02(6)	H(11)–C(1)–H(13)	107.4(22)	H(32)–C(3)–H(33)	107.6(20)
N(1)–Si(1)–C(2)	113.93(6)	H(12)–C(1)–H(13)	111.7(24)	N(1)–C(4)–H(41)	110.5(14)
N(1)–Si(1)–C(3)	108.89(6)	Si(1)–C(2)–H(21)	112.7(15)	N(1)–C(4)–H(42)	107.9(16)
C(1)–Si(1)–C(2)	108.03(7)	Si(1)–C(2)–H(22)	108.5(16)	N(1)–C(4)–H(43)	113.5(13)
C(1)–Si(1)–C(3)	109.90(7)	Si(1)–C(2)–H(23)	111.7(13)	H(41)–C(4)–H(42)	110.1(21)
C(2)–Si(1)–C(3)	108.04(6)	H(21)–C(2)–H(22)	106.9(21)	H(41)–C(4)–H(43)	109.7(18)
Si(1)–N(1)–C(4)	122.92(10)	H(21)–C(2)–H(23)	106.6(20)	H(42)–C(4)–H(43)	105.0(20)
Si(1)–N(1)–C(5)	122.91(10)	H(22)–C(2)–H(23)	110.2(20)	N(1)–C(5)–H(51)	114.1(14)
C(4)–N(1)–C(5)	111.95(12)	Si(1)–C(3)–H(31)	106.7(13)	N(1)–C(5)–H(52)	114.5(13)
Si(1)–C(1)–H(11)	108.2(15)	Si(1)–C(3)–H(32)	111.9(13)	N(1)–C(5)–H(53)	105.3(12)
Si(1)–C(1)–H(12)	111.8(18)	Si(1)–C(3)–H(33)	111.9(15)	H(51)–C(5)–H(52)	101.7(19)
Si(1)–C(1)–H(13)	109.9(16)	H(31)–C(3)–H(32)	106.8(18)	H(51)–C(5)–H(53)	111.8(18)
H(11)–C(1)–H(12)	107.7(23)	H(31)–C(3)–H(33)	111.8(20)	H(52)–C(5)–H(53)	109.5(18)

Table 3. Weighting functions, correlation parameters, and scale factors for $NMe_2(SiMe_3)$

Camera height/ mm	λ/Å	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor
		nm^{-1}						
128.4	0.057 17	4	60	80	300	340	−0.020	0.822(20)
285.7	0.057 13	2	20	40	120	144	0.451	0.692(10)

Joyce-Loebl microdensitometer[10] and electron wavelengths were determined from the diffraction patterns of gaseous benzene, recorded on the same occasions as the sample data. Calculations were performed with ICL 2972 computers using established data-reduction[10] and least-squares refinement[11] programs. Table 3 lists weighting points used in setting up the off-diagonal weight matrices, together with other data relevant to the diffraction experiment. The complex scattering factors of Schäfer *et al.*[12] were employed in all calculations. The observed combined molecular-scattering intensities for $NMe_2(SiMe_3)$ are shown in Figure 1 and the corresponding observed radial distribution curve in Figure 2.

In the molecular model local C_{3v} symmetry was assumed for all methyl groups and local C_3 symmetry for the $SiMe_3$ group. The structure was described by four bonded distances (all C–H bonds were considered equal in length), five valence angles (SiNC, NSiC, CNC, NCH, and SiCH), twist angles for the Si-methyl and the N-methyl groups, and a twist and a tilt of the $SiMe_3$ group. The Si-methyl twist was defined to be zero when one C–H bond was *anti* with respect to the Si–N bond and was positive for clockwise rotation when viewed from carbon to silicon. The N-methyl twist was zero when one C–H bond was *anti* with respect to the more distant N–C bond and was positive for clockwise rotation viewed along the C–N bond, towards nitrogen. The $SiMe_3$ tilt angle was defined as the angle between the local C_3 axis of the $SiMe_3$ group and the Si–N bond. The direction and sign of the tilt were such that a positive tilt for a structure with zero $SiMe_3$ twist resulted in the movement of the methyl group lying in the plane of symmetry of the molecule away from the NMe_2 group.

Refinement of gas phase structure. The radial distribution curve (Figure 2) shows three peaks below 2 Å. The largest at 1.85 Å arises from the overlap of the Si–N and Si–C distances. However, this did not prove to be a problem and all four bond lengths and associated amplitudes of vibration and all five valence angles refined satisfactorily. There were no severe correlations between these parameters, as can be seen from the portion of the correlation matrix reproduced in Table 4.

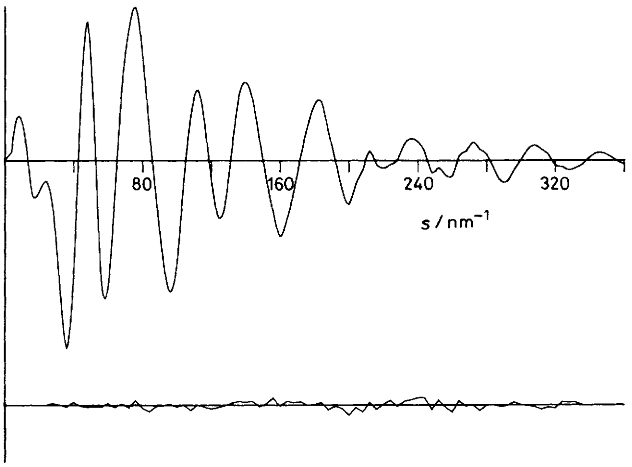

Figure 1. Observed and final weighted difference combined molecular scattering intensities for $NMe_2(SiMe_3)$

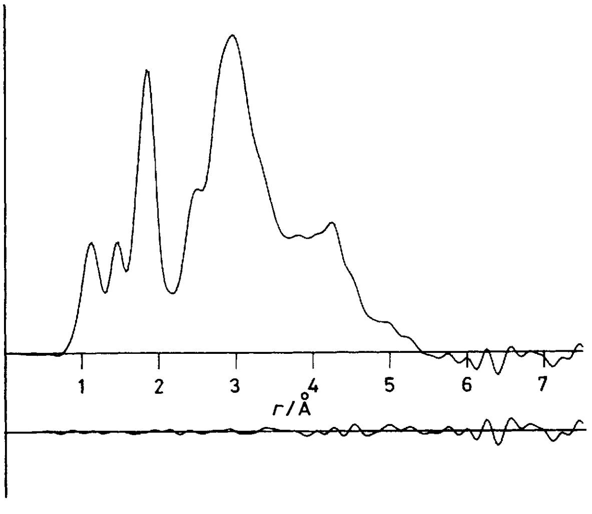

Figure 2. Observed and final difference radial distribution curves, $P(r)/r$, for $NMe_2(SiMe_3)$. Before Fourier inversion the data were multiplied by $s\exp(-0.000\,02\,s^2)/(Z_{Si}-f_{Si})(Z_C-f_C)$

Starting values for refinement of the twist angles were determined by varying each angle stepwise over a range of values. The parameters were set at those values which gave the minimum R factors and were subsequently refined. As the N-methyl twist consistently refined to zero it was fixed at this value.

Table 4. Portion of least-squares correlation matrix (× 100) for $NMe_2(SiMe_3)$*

	r_3	a_4	u_1	u_5	u_6	k_2
r_1	58					
a_1					55	
a_2					56	
a_3	70	63				
a_7				−56	−51	
u_3			75			52
u_4						70
u_5					72	

* Only elements with absolute values ≥50 are included.

Table 5. Molecular (independent) parameters[a]

r_1(Si–N)/Å	1.710(5)
r_2(N–C)/Å	1.462(4)
r_3(Si–C)/Å	1.868(4)
r_4(C–H)/Å	1.107(4)
a_1(SiNC)/°	121.4(5)
a_2(NSiC)/°	110.3(7)
a_3(NCH)/°	107.5(14)
a_4(SiCH)/°	108.1(8)
a_5(CNC)/°	117.1(10)[b]
a_6(N–CH_3 twist)/°	0.0 (fixed)
a_7(Si–CH_3 twist)/°	−12.1(45)
a_8[Si$(CH_3)_3$ twist]/°	9.6(20)
a_9[Si$(CH_3)_3$ tilt]/°	0.0 (fixed)

[a] Parameters are r_a; errors quoted in parentheses are estimated standard deviations obtained in least-squares analyses, increased to allow for systematic errors. [b] Once planarity at nitrogen was established the CNC angle was defined as 360 − 2(SiNC)°.

Table 6. Interatomic distances (r_a/Å) and amplitudes of vibration (u/Å)[a]

	Distance	Amplitude
r_1 (Si–N)	1.710(5)	0.053(5)
r_2 (N–C)	1.462(4)	0.053(4)
r_3 (Si–C)	1.868(4)	0.062(4)
r_4 (C–H)	1.107(4)	0.087(4)
r_5 [Si(N)C]	2.770(7)	0.086(8)
r_6 [N(Si)C]	2.939(13)	0.104(19)
r_7 [N(C)H]	2.083(22)	0.118(22)
r_8 [H(C)H]	1.829(17)	0.105[b]
r_9 [Si(C)H]	2.450(13)	0.107[b]
r_{10}[C(N)C]	2.494(16)	0.100[b]
r_{11}[C(Si)C]	3.034(14)	0.100[b]
r_{12}[C(SiN)C]	3.886(22)	0.100[b]
r_{13}[C(SiN)C]	4.212(19)	0.124[c]
r_{14}[C(SiN)C]	3.205(27)	
r_{15}[C(SiN)C]	3.693(30)	
r_{16}[C(SiN)C]	3.318(24)	
r_{17}[C(SiN)C]	4.298(13)	

[a] Other Si ··· H, N ··· H, C ··· H, and H ··· H distances were included in the refinements but are not listed here. [b] Amplitude refined and fixed. [c] Amplitudes refined as a group and fixed.

In the early refinements the tilt angle of the $SiMe_3$ group had been held at zero while the geometry at nitrogen was being investigated. Under these conditions the sum of angles at nitrogen consistently refined to 360°. It seemed possible, however, that the geometry at nitrogen and the tilt angle could be correlated and consequently a series of refinements was done to test this. With no geometrical constraint at nitrogen the tilt angle was systematically varied from −5 to +5°. The results showed a clear correlation. When the tilt angle was zero the sum of angles at nitrogen was 360.0(15)°. As the tilt angle increased in either direction the geometry at nitrogen became increasingly non-planar. At +5° the sum of angles at nitrogen was 356.7(45)°. The R factor range was such that the 95% confidence limit was reached at ±3°. A shallow minimum at $R_G = 0.0887$ was obtained at +1°, at which point the sum of angles at nitrogen equalled 359.9(25)°. The other parameters did not vary significantly, other than the twist angle of the silicon methyl groups which varied from −20° to zero and became very poorly defined. Final refinements were performed with the model modified to impose planarity at nitrogen and with the tilt angle fixed at zero. The Si-methyl twist refined satisfactorily to −12.1(45)°, estimated standard deviations (e.s.d.s) in general were improved and the final R_G factor was 0.0867. Thus the best fit to the data was obtained with the $NMe_2(SiMe_3)$

Table 7. Geometrical parameters: distances (Å) and angles (°) for $NMe_2(SiH_nMe_{3-n})$ (n = 0—3)

	$NMe_2(SiMe_3)$ (solid)	$NMe_2(SiMe_3)$ (gas)	$NMe_2(SiHMe_2)$[a] (gas)	$NMe_2(SiH_2Me)$[a] (gas)	$NMe_2(SiH_3)$[a] (gas)
Si–C	1.863[b]	1.868(4)	1.869(3)	1.867(6)	
Si–N	1.7194(12)	1.710(5)	1.719(5)	1.715(6)	1.713(5)
N–C	1.448[b]	1.462(4)	1.460(4)	1.455(3)	1.457(6)
CNC	111.95(12)	117.1(10)	113.7(15)	112.7(8)	112.0(6)
CNSi	122.9[b]	121.4(5)	119.3(8)	121.5(8)	120.9(3)
NSiC	110.3[b]	110.3(7)	109.9(18)	113.3(23)	
CSiC	108.7[b]	108.7(7)	107.5(38)		
Sum of angles round nitrogen	357.78(18)	360[c]	352.4(18)	355.6(15)	354.6(7)

[a] Data from ref. 5. [b] Mean value. [c] Fixed.

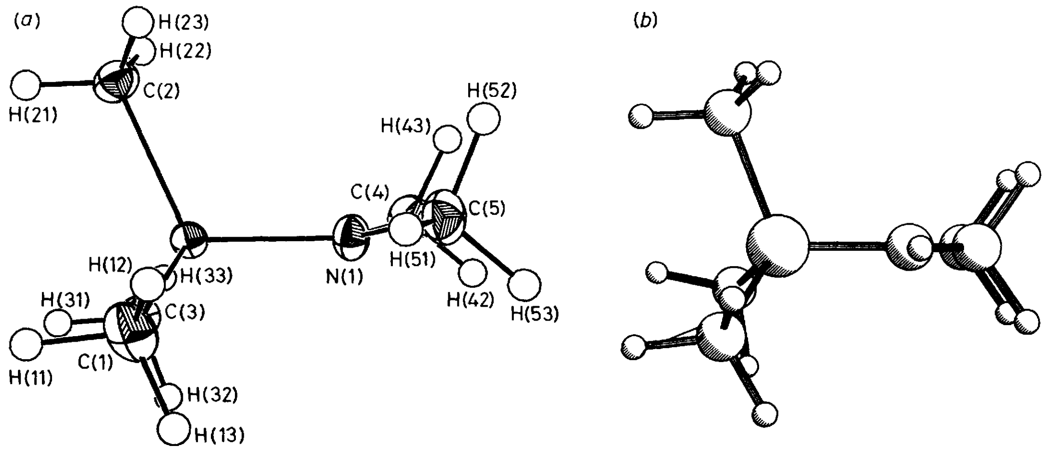

Figure 3. Perspective views of $NMe_2(SiMe_3)$ in (*a*) the crystal phase [H(41) totally obscured] and (*b*) the gas phase

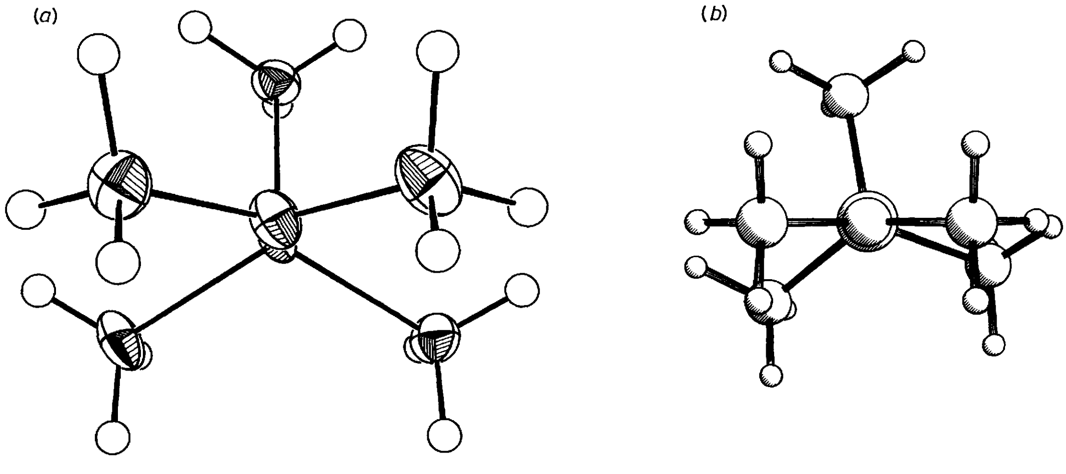

Figure 4. The crystal structure (*a*) and the gas phase structure (*b*) of $NMe_2(SiMe_3)$ viewed from nitrogen towards silicon

molecule planar at nitrogen and with the $SiMe_3$ group untilted. However, the possibility that the molecule has a very small $SiMe_3$ tilt and is not completely planar at nitrogen cannot be entirely ruled out. The final values of the parameters, interatomic distances and amplitudes of vibration are given in Tables 5 and 6.

Results and Discussion

As can be seen from Table 7, and from Figures 3 and 4 which show perspective views of $NMe_2(SiMe_3)$ in both gas and crystal phases, the results from the electron diffraction and from the crystallographic structure determination are in good agreement. The one major difference is that the CNC angle is considerably larger in the gas phase, and, as the SiNC angles are very similar in both studies, the geometry at nitrogen is planar in the gas but very slightly pyramidal in the crystal. Although the best fit to the gas phase data was for a planar structure the studies of the correlation between the $SiMe_3$ tilt and planarity at nitrogen showed that some distortion could not be discounted. The extent of this possible distortion was sufficient (at the 95%

confidence limit) to include a structure comparable to that found in the crystal.

The solid structure consists of molecules with non-crystallographic C_s symmetry essentially isolated from each other: in particular, there are no close Si $\cdots$ N intermolecular contacts. The distortions from ideal geometry (planar at N, tetrahedral at Si) are a tilting of the NMe$_2$ group towards the unique Si-bonded carbon C(2) and a widening of the C(2)SiN angle. The bond to C(2) is the longest Si–C bond (Table 2). In the gas phase the molecules are distorted from C_s symmetry by a slight twist of the SiMe$_3$ group around the Si–N bond and by a small twist of the methyl groups on silicon. The twist angle of the SiMe$_3$ group may in fact be zero in the average structure with the observed deviation being a shrinkage effect arising from torsional vibrations.

The values for the bonded distances are much as would be expected. The Si–N bond is short in comparison with the values found for di- and tri-silylamines (1.73—1.75 Å). This is a characteristic feature of dimethyl(silyl)amines as can be seen from Table 7 which includes gas phase structural parameters for the other three members of the series NMe$_2$(SiH$_n$Me$_{3-n}$) (n = 0—3). It is surprising how little effect increased methylation at silicon has on the bond lengths and on most angles: this implies that steric influences on these parameters are minimal. There are minor variations in the angles NSiC and CNSi but no trends are apparent, whereas increasing methylation does correlate with a widening of the CNC angle in the gas phase. The solid state CNC angle for NMe$_2$(SiMe$_3$), however, is no greater than that found for NMe$_2$(SiH$_3$).

Some extended Hückel molecular orbital calculations have been performed with parameters as specified in SUP 56368 to investigate the energy differences between an idealised model for NMe$_2$(SiMe$_3$) and models incorporating various distortions. These included tilting of the NMe$_2$ group towards silicon, rotation of the SiMe$_3$ group about the Si–N bond, and systematic variation of the CNC angle. Although such calculations clearly have their limitations the results did confirm what we had suspected: that the potentials for all these distortions are very shallow with very small energy barriers. Thus the NMe$_2$(SiMe$_3$) molecules [and almost certainly the other dimethyl(silyl)amines as well] are easily deformed or 'floppy'. In the vapour the nitrogen adopts a planar co-ordination whereas in the solid the crystal packing forces are enough to tip the balance in favour of a smaller CNC angle and slight non-planarity at nitrogen. There is distortion of the SiMe$_3$ group from perfect C_3 symmetry and the group is also slightly tilted away from the NMe$_2$ group. The question remains whether the observed non-planarity at nitrogen in NMe$_2$(SiHMe$_2$), NMe$_2$(SiH$_2$Me), and NMe$_2$(SiH$_3$) represents potential minima, or average values for planar molecules vibrating with very large amplitudes. What is clear, however, is that the dimethyl(silyl)amines, as a group, fit into a logical progression between truly pyramidal trimethylamine and the truly planar methyldi(silyl)amines.

Sometimes p_π–d_π bonding is invoked to rationalise geometrical features of silylamines. It is certainly a plausible explanation for the short Si–N bonds in the di- and tri-silylamines, in which the nitrogen lone-pair electrons have to be shared between two and three bonds. Extended Huckel calculations were performed to investigate the role of the Si d orbitals in the overall bonding scheme in NMe$_2$(SiMe$_3$). The effect of including Si 3d orbitals in the calculations was considerable; inclusion resulted in a stronger, less polar Si–N bond as a direct consequence of *ca.* 0.14 e being transferred from N 2p_x to Si 3d_{xz} (SiNC$_2$ fragment in yz plane with SiN bond parallel to z axis). Moreover, including Si 3d orbitals stabilises the molecule by *ca.* 170 kJ mol^{-1}.

Acknowledgements

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