

Determination of the Molecular Structure of Dimethyl(silyl)amine, Dimethyl(methylsilyl)amine and Dimethyl(dimethylsilyl)amine in the Gas Phase by Electron Diffraction

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New studies of $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$ and $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$ and a reinvestigation of $\text{SiH}_3\text{N}(\text{CH}_3)_2$ show that the nitrogen atom in these dimethylsilylamines has a shallow pyramidal configuration in agreement with the earlier study of the last compound: the sum of angles are $352.4(18)$, $355.6(15)$ and $354.6(7)^\circ$, respectively. The important bond distances (r_a) and valence angles (\angle_a ; no shrinkage correction was applied) are: $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$, N-C 146.0(4) pm, C-N-C $113.7(15)^\circ$, Si-N-C $119.3(8)^\circ$, Si-N 171.9(5) pm, Si-C 186.9(3) pm, N-Si-C $109.9(18)^\circ$ and C-Si-C $107.5(38)^\circ$; $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$, N-C 145.5(3) pm, C-N-C $112.7(8)^\circ$, Si-N-C $121.5(8)^\circ$, Si-N 171.5(6) pm, Si-C 186.7(6) pm and N-Si-C $113.3(23)^\circ$; and $\text{SiH}_3\text{N}(\text{CH}_3)_2$, N-C 145.7(6) pm, C-N-C $112.0(6)^\circ$, Si-N-C $120.9(3)^\circ$ and Si-N 171.3(5) pm. The preferred conformations of the two first compounds have one Si-CH₃ bond *gauche* to the lone pair of electrons on the nitrogen atom and the close C-N-Si-C angles are $68(6)$ and $50(5)^\circ$ for $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$ and $72(3)^\circ$ for $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$.

We are presently studying the molecular structures of several methyl derivatives of mono(silyl), bis(silyl) and tris(silyl)amines. In particular, we hope to gain information on how the Si-N bond lengths and other parameters vary in such series of corresponding silylamines, and on structural

variations within each class as methyl substitution is increased. In this paper we report results from gas-phase electron-diffraction studies of $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$ and $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$ [hereafter denoted MH2 and MH1, respectively]. In these compounds the conformation is also of importance, in particular in relation to the configuration at nitrogen, which may be planar or non-planar. In fact, most structures of such compounds have a planar skeleton, but dimethylsilylamine is slightly pyramidal [angle sum around nitrogen is $351.1(2)^\circ$] in the gas phase according to an electron-diffraction study.¹ Vibrational spectroscopic data^{2,3} for this compound in the gas phase indicate that it has non-planar structure and X-ray data show that it is pentametric in the crystalline phase.⁴ A reinvestigation of $\text{SiH}_3\text{N}(\text{CH}_3)_2$ [hereafter denoted MH3] by gas-phase electron diffraction is included in the present study so that consistent structural data are available for the whole series MH3 to MH1.

EXPERIMENTAL

Samples of MH3, MH2 and MH1 were prepared by gas-phase reactions of dimethylamine with appropriate silylhalides: SiBrH_3 for MH3;⁵ SiClH_2Me for MH2 (instead of SiH_2Ime as in an earlier preparation⁶); and SiClHMe_2 for MH1. The compounds were purified by repeated fractional condensations in the vacuum system, and the purity of each sample was checked by i.r. spectroscopy. Vapour pressures at 273 K were *ca.* 120 and 45 torr for MH2 and MH1, respectively.

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Electron-diffraction scattering intensities were recorded on Kodak Electron Image plates, using the Edinburgh diffraction apparatus^{7,8} with nozzle-to-plate distances of 128 and 286 mm and an accelerating voltage of *ca.* 44 kV. During expo-

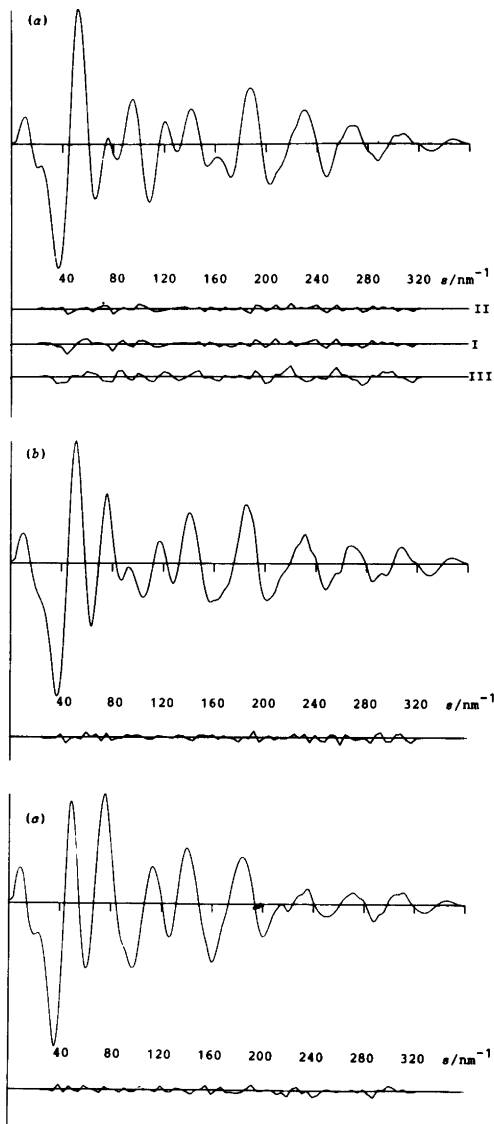


Fig. 1. Observed and final weighted difference combined molecular scattering intensities for (a) $\text{SiH}_3\text{N}(\text{CH}_3)_2$, (b) $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$ and (c) $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$. In (a) difference curves for three refinements I, II and III (*cf.* Table 2) are given and II corresponds to the preferred structure.

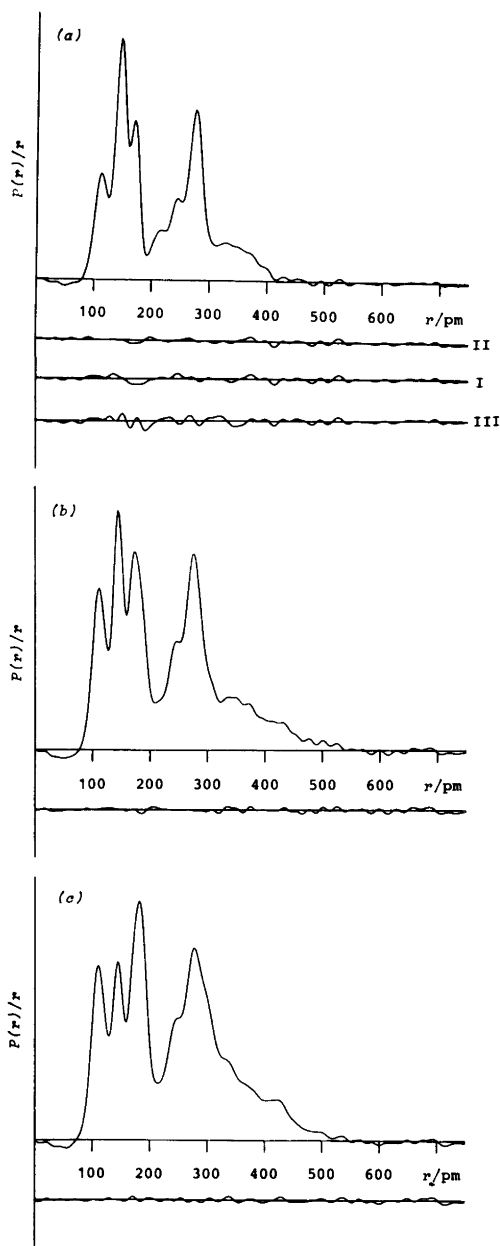


Fig. 2. Observed and final difference radial-distribution curves, $P(r)/r$, corresponding to the intensities given in Fig. 1: (a) $\text{SiH}_3\text{N}(\text{CH}_3)_2$, (b) $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$ and (c) $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$. In each case, before Fourier inversion, the data were multiplied by $s \cdot \exp(-0.00002s^2)/(Z_{\text{Si}} - f_{\text{Si}})(Z_{\text{C}} - f_{\text{C}})$.

Table 1. Weighting functions, correlation parameters, and scale factors.

Compound	Camera height mm	Wave-length pm	Δs nm ⁻¹	s_{\min}	sw_1	sw_2	s_{\max}	Correlation parameter	Scale factor
SiH ₃ N(CH ₃) ₂ ^a	128.4	5.675	4	60	80	300	324	-0.111	0.754(29)
	285.8	5.673	2	20	40	120	140	0.487	0.874(20)
CH ₃ SiH ₂ N(CH ₃) ₂	128.4	5.680	4	60	88	300	328	-0.212	0.621(25)
	285.8	5.680	2	20	40	120	140	0.405	0.745(15)
(CH ₃) ₂ SiHN(CH ₃) ₂	128.4	5.679	4	60	80	300	324	0.041	0.807(23)
	285.6	5.679	2	20	40	120	140	0.325	0.749(16)

^a Refinement II of Table 2.

tures, the nozzle was maintained at room temperature [295 K] and the samples of MH3 and MH1 at 295 K and MH2 at 273 K. Data were obtained in digital form using a computer-controlled Joyce-Loebl microdensitometer with the scanning programme described previously.⁹ Electron wavelengths were determined from the scattering patterns of gaseous benzene, recorded on the same occasions as the sample data.

Calculations were carried out on ICL-2972 computers using established data-reduction⁹ and least-squares refinement¹⁰ programs. Weighting points used in setting up the off-diagonal weight matrices are given, together with other pertinent data, in Table 1. In all calculations the complex scattering factors of Schäfer *et al.* were used.¹¹

The observed combined molecular-scattering intensities for MH3, MH2 and MH1 are shown in Fig. 1 and the corresponding observed radial-distribution curves are shown in Fig. 2.

GEOMETRICAL MODELS

Views of the molecules showing the atom numbering are presented in Figs. 3 and 4. The final geometrical parameters are given in Tables 2, 3 and 4 for MH3, MH2 and MH1, respectively. The torsional (dihedral) angles are defined relative to zero for *syn* conformation and they are positive for counterclockwise rotation.

In each case the Si-NC₂ skeleton was assumed to have C_s-symmetry and was described by $r(\text{Si-N})$, $r(\text{N-C})$, $\angle(\text{Si-N-C})$, and $\angle(\text{C-N-C})$ thus allowing for pyramidal configuration at the nitrogen atom. The nonplanarity was visualized by a 'dip'-angle [β], defined as the angle between the bisector of $\angle(\text{C-N-C})$ and the extension of the Si-N bond, and by the sum of the three angles around the nitrogen atom [α],

both introduced as dependent angles in Tables 2 to 4. An option was provided to impose coplanarity about nitrogen [*i.e.* $\alpha=360^\circ$, $\beta=0^\circ$].

The overall conformations of the molecules were defined by the torsional angle, $\phi(\text{Si-N})$ defined with respect to the bisector (b) of the C-N-C angle and (if any) the unique substituent of silicon, *i.e.* $\phi(\text{H1-Si-N-b})$, $\phi(\text{C3-Si-N-b})$ and $\phi(\text{H1-Si-N-b})$, respectively for MH3, MH2, and MH1 [see Fig. 4]. The $\phi(\text{Si-N})$ values are thus zero for staggered conformation of Si(H/R)₃-NC₂E where E denotes the lone pair of electrons of nitrogen in a pyramidal configuration.

The torsion angles of the N-methyl groups were defined with respect to the (CH₃)₂N-moiety of the molecules, *i.e.* by $\theta_1=\theta(\text{H-C1-N-C2})$ and $\theta_2=\theta(\text{H-C2-N-C1})$, and these angles could be treated as independent parameters, or constrained to be equal giving local C₂-symmetry for the -N(CH₃)₂ group. The relation $\theta_2=\theta_1-60^\circ$ was also permitted, but it became clear that the C₂ model with H-C-N-C angles close to 60° was favoured. [Tables 2 to 4].

All the X-CH₃ [X=N,Si] groups were assumed to have local C_{3v} symmetry. In the preliminary analyses of MH2 and MH1 the C-H bonded distances of N-CH₃ and Si-CH₃ were allowed to be of different length, but this distinction proved to be of no significance and in the final refinements all the C-H bonds were assumed to be equal in length.

For MH3 [Table 2] N-SiH₃ was assumed to have local C_{3v} symmetry, whereas the N-SiH₂C fragment in MH2 [Table 3] had C_s-symmetry. In the latter molecule the H-Si-H plane could be constrained to bisect the N-Si-C angle or it

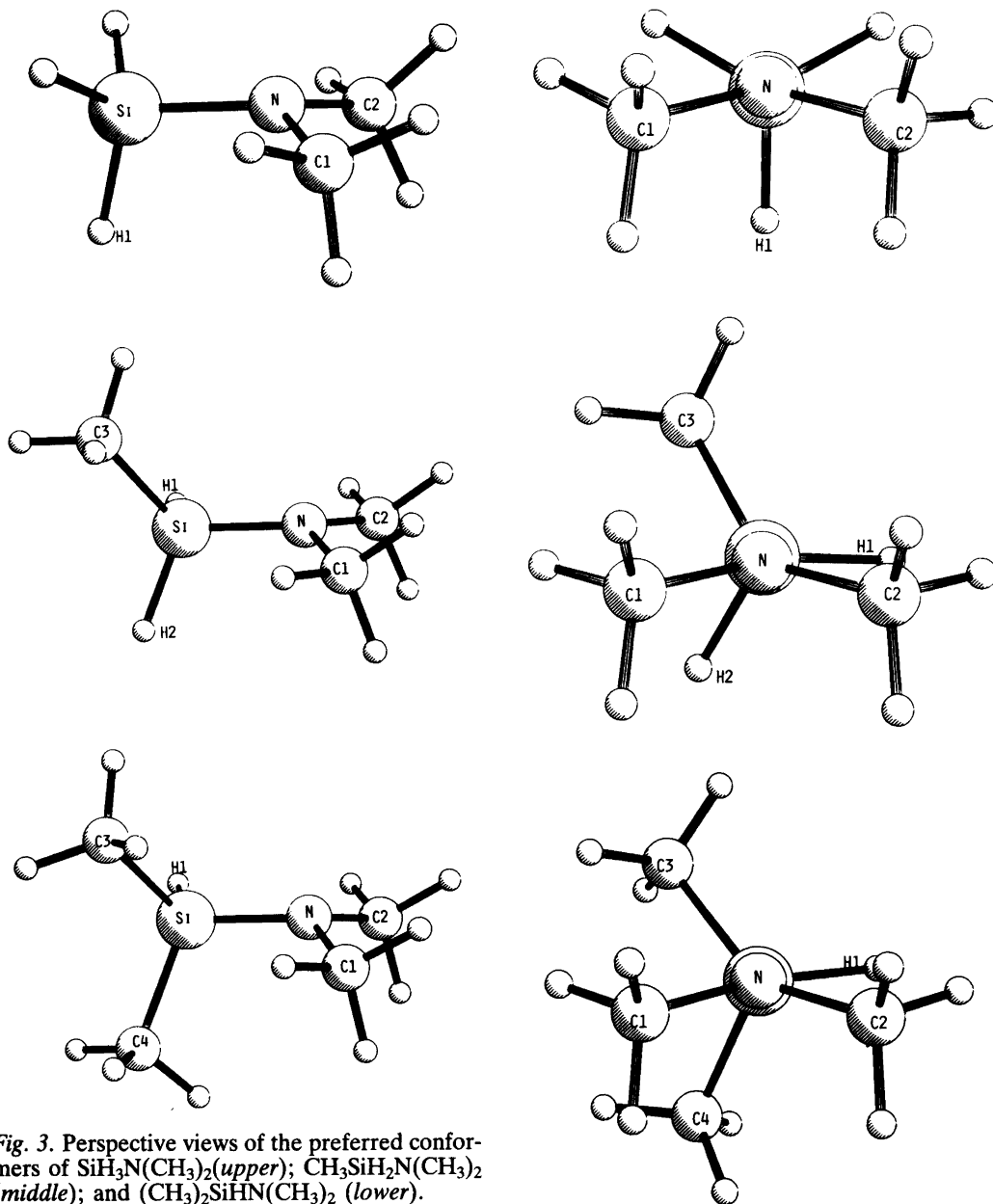


Fig. 3. Perspective views of the preferred conformers of $\text{SiH}_3\text{N}(\text{CH}_3)_2$ (upper); $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$ (middle); and $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$ (lower).

could be tilted from this position. As angular arrangements of the bonds to silicon appear to be rather flexible, the possibility that the $\text{N}-\text{SiC}_2\text{H}$ fragment in MH1 had $\text{N}-\text{Si}-\text{C}$ angles of different magnitudes was considered, but C_s -symmetry was adopted for the final refinements in which

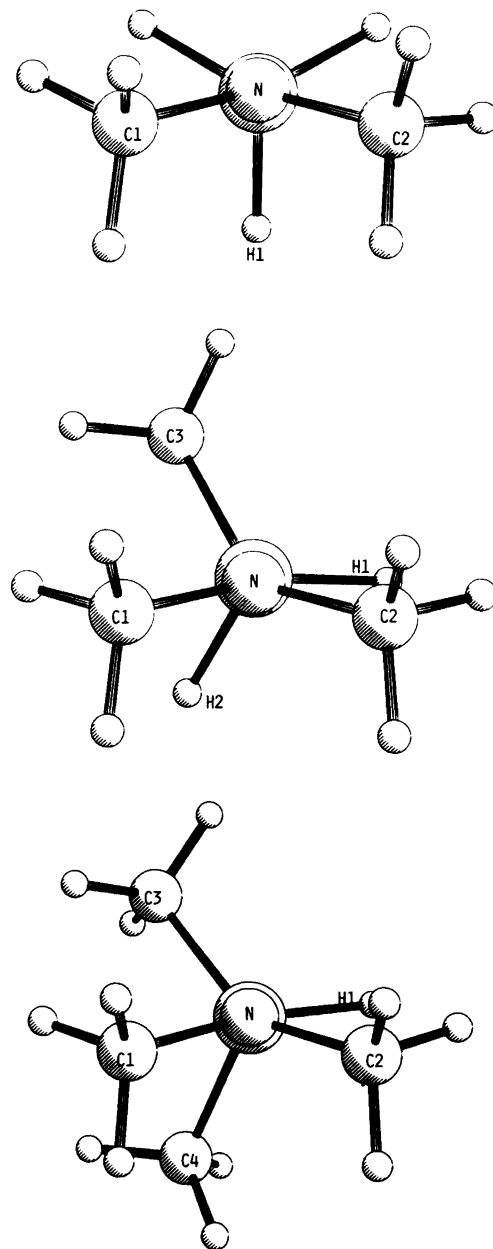


Fig. 4. Views of the molecules shown in Fig. 3 along their $\text{Si}-\text{N}$ bonds: $\text{SiH}_3\text{N}(\text{CH}_3)_2$ (upper); $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$ (middle); and $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$ (lower).

case the a_6 -parameter [Table 4] is equal to half the $\text{C}-\text{Si}-\text{C}$ angle.

Table 2. Molecular parameters (r_a , \angle_a) for $\text{SiH}_3\text{N}(\text{CH}_3)_2$.

	Previous Ref. 1	This work I	II ^a	III
Independent distances/pm			(Preferred)	(Planar skeleton enforced)
$r_1(\text{C-H})$	108.4(8)	112.1(5)	111.8(6)	111.8(8)
$r_2(\text{Si-H})$	148.5(fixed)	148.5(fixed)	146.6(19)	148.5(fixed)
$r_3(\text{C-N})$	146.2(4)	145.5(3)	145.7(6)	144.7(4)
$r_4(\text{Si-N})$	171.4(4)	171.3(3)	171.3(5)	170.5(5)
Independent angles/°				
$a_1(\text{SiNC})$	120.0(4)	121.3(3)	120.9(3)	122.9(3)
$a_2(\text{CNC})$	111.1(12)	111.9(6)	112.0(6)	[116.2] ^c
$a_3(\text{NCH})$	109.5(fixed)	109.5(fixed)	110.5(10)	109.5(fixed)
$a_4(\text{H-C-N-C})$	60.0(fixed)	60.0(fixed)	49.0(16)	60.0(fixed)
$a_5(\text{NSiH})$	109.5(fixed)	109.5(fixed)	107.2(30)	109.5(fixed)
$a_6(\text{Si-N twist})$	0. (fixed)	0. (fixed)	0. (fixed)	0. (fixed)
Dependent angles/ ^{ob}				
α	351.1(20)	354.6(7)	353.9(8)	360. (fixed)
β	27.8(20)	22.0(16)	23.2(18)	0. (fixed)
$\theta(\text{H-Si-N-C})$	—	75.8(10)	75.1(12)	90. (fixed)

^a Corresponding interatomic distances and correlation matrix are given in Tables 5 and 8, respectively. ^b α is the sum of angles about nitrogen; β is the dip angle defined in the text. ^c Dependent parameter.

The conformation of the Si-methyl group in MH2 [Table 3] was defined with respect to the N-Si-CH₃ arrangement, *i.e.* by $\theta_3 = \theta(\text{H-C}_3\text{-Si-N})$. The two Si-CH₃ torsional parameters of MH1 were defined within the Si(CH₃)₂ moiety, *i.e.* $\theta_3 = \theta(\text{H-C}_3\text{-Si-C}_4)$ and $\theta_4 = \theta(\text{H-C}_4\text{-Si-C}_3)$. They were treated analogously to the θ_1 and θ_2 parameters of N(CH₃)₂ and the option $\theta_3 = \theta_4$ was used in the final refinement [a_9 , Table 4].

STRUCTURE ANALYSIS AND RESULTS

a. Silyldimethylamine (MH3). Two of the four types of bond distances (Table 5), are resolved in the radial-distribution curve [Fig. 2(a)]: the C-H distances at 110 pm and the Si-N distance at about 170 pm. The N-C and Si-H bonds contribute in the ratio *ca.* 2:1 to the peak at *ca.* 145 pm. The one-angle N...H (methyl) distances account for the feature at 215 pm and a large contribution from the Si...C distances is clearly responsible for the prominent peak at 275 pm. Thus, the C...C and N...H (silyl) distances must account for the feature preceding the large peak

at 275 pm contributing *ca.* 60 and 40 %, respectively. The remaining significant contributions are from C...H (methyl), Si...H (methyl) and C...H (silyl) distances which account mainly for the area beyond $r=275$ pm. The first two of these depend on the methyl twist parameters and the C₂-model. [$a_4 = \theta_1 = \theta_2$, Table 2] appeared to be favoured. The last of the three types of distances depends on the $\theta(\text{Si-N})$ parameter, which was finally assumed to be 0°: the optimum value was actually 15°, but the improvement gained by using this angle was insignificant.

A refinement with the same assumptions as were used in the previous study¹ was carried out, and the results of the two refinements are compared in Table 2 [Previous and I]. The new results have better least-squares agreement factors [R_G/R_D -values are 11.6/8.5 % compared to 15.0/11.0 % formerly] and more reasonable values for u_1 and u_4 . In both cases the refined nitrogen configuration is pyramidal [*cf.* the α and β values in Table 2], but somewhat less in the present investigation.

Subsequent refinement of the structure gave $\theta(\text{N-CH}_3)$ and $\angle(\text{N-C-H})$ values of 41(7)° and

Table 3. Molecular parameters (r_a , \angle_a) for $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$.^a

Independent distances/pm	
$r_1(\text{C}-\text{H})$	111.6(5)
$r_2(\text{Si}-\text{H})$	148.5(fixed)
$r_3(\text{C}-\text{N})$	145.5(3)
$r_4(\text{Si}-\text{N})$	171.5(6)
$r_5(\text{Si}-\text{C})$	186.7(6)
Independent angles/°	
$a_1(\text{SiNC})$	121.5(8)
$a_2(\text{CNC})$	112.7(8)
$a_3(\text{NCH})$	113.4(24)
$a_4(\text{H}-\text{C}-\text{N}-\text{C})$	60.0(fixed)
$a_5(\text{NSiC})$	113.3(23)
$a_6(\text{HSiH})$	108.5(fixed)
$a_7(\text{SiCH})$	113.4(30)
$a_8(\text{H}-\text{C}-\text{Si}-\text{N})$	60.0(fixed)
$a_9(\text{Si}-\text{N}, \text{twist})$	-149.8(30)
Dependent angles/°	
$a(\text{NSiH})$	108.7-
$a(\text{CSiH})$	108.7-
$\alpha(a_2+2a_1)$	355.6(15)
$\beta(\text{dip})$	19.6(30)
$\theta(\text{C1}-\text{N}-\text{Si}-\text{C3})$	-72.4(30)
$\theta(\text{C2}-\text{N}-\text{Si}-\text{C3})$	+132.9(39)
$\theta(\text{C1}-\text{N}-\text{Si}-\text{H1})$	+166.6-
$\theta(\text{C1}-\text{N}-\text{Si}-\text{H2})$	+48.6-
$\theta(\text{C2}-\text{N}-\text{Si}-\text{H1})$	-11.8-
$\theta(\text{C2}-\text{N}-\text{Si}-\text{H2})$	+106.1-

^a Corresponding distance list and correlation matrix are given in Tables 6 and 9, respectively. See text for definition of β , and a_9 .

111.1(10)°, respectively and R_G/R_D values of 10.2/8.3 %. This stage of the structure analysis was hampered by difficulties in locating the silyl hydrogen atoms. The problem arises from the overlaps of the Si-H and N...H (silyl) distances with the skeletal N-C and C...C distances, respectively. Each of the contributions involving the hydrogen atoms is of minor importance, thus making the refinement of $r(\text{Si}-\text{H})$ and $\angle(\text{N}-\text{Si}-\text{H})$ difficult. Typically, for $\angle(\text{N}-\text{Si}-\text{H})=109.5^\circ$ $r(\text{Si}-\text{H})$ was 146(2) pm or less, whereas a length of 148.5 pm for the Si-H bond gave an angle of about 96(2)°. Table 2, column II contains the results of a refinement in which the two parameters in question refined to reasonable values, with fairly large standard deviations. The corresponding R_G/R_D -values were 9.8/7.4 %.

Table 4. Molecular parameters (r_a , \angle_a) for $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$.^a

Independent distances/pm	
$r_1(\text{C}-\text{H})$	111.5(5)
$r_2(\text{Si}-\text{H})$	148.5(fixed)
$r_3(\text{C}-\text{N})$	146.0(4)
$r_4(\text{Si}-\text{N})$	171.9(5)
$r_5(\text{Si}-\text{C})$	186.9(3)
Independent angles/°	
$a_1(\text{SiNC})$	119.3(8)
$a_2(\text{CNC})$	113.7(15)
$a_3(\text{NCH})$	111.5(fixed)
$a_4(\text{H}-\text{C}-\text{N}-\text{C})$	60.0(fixed)
$a_5(\text{NSiC})$	109.9(18)
$a_6(\text{Si}-\text{C}/\text{NSiH})$	53.7(20)
$a_7(\text{NSiH})$	109.5(fixed)
$a_8(\text{SiCH})$	107.6(20)
$a_9(\text{H}-\text{C}-\text{Si}-\text{C})$	-37.2(70)
$a_{10}(\text{Si}-\text{N}, \text{twist})$	+97.3(46)
Dependent angles/°	
$a(\text{C}-\text{Si}-\text{C})$	107.5(38)
$a(\text{CSiH})$	110.0-
$\alpha(a_2+2a_1)$	352.4(18)
$\beta(\text{dip})$	26.5(24)
$\theta(\text{C1}-\text{N}-\text{Si}-\text{C3})$	-68.0(59)
$\theta(\text{C1}-\text{N}-\text{Si}-\text{C4})$	+50.1(47)
$\theta(\text{C2}-\text{N}-\text{Si}-\text{C3})$	+144.5(56)
$\theta(\text{C2}-\text{N}-\text{Si}-\text{C4})$	-97.4(46)
$\theta(\text{C1}-\text{N}-\text{Si}-\text{H1})$	+171.0-
$\theta(\text{C2}-\text{N}-\text{Si}-\text{H1})$	+23.6-

^a Corresponding distance list and correlation matrix are given in Tables 7 and 10, respectively. See text for definitions of a_6 , a_{10} and β .

The amplitude of vibration [Table 5] associated with the C...C distance is low [5.6(12) pm], but it agrees with the value of 5.8(14) pm obtained in the previous study, and spectroscopic and electron-diffraction $u(\text{C}\cdots\text{C})$ values for $\text{N}(\text{CH}_3)_3$ are in the range 5.9-7.4 pm.¹²

The various combinations of values obtained for $r(\text{Si}-\text{H})$ and $\angle(\text{N}-\text{Si}-\text{H})$ give N...H (silyl) distances in the range of 240-263 pm. The uncertainty about these parameters is unfortunate since it may affect the location of the C...C distance and hence the determination of $\angle(\text{C}-\text{N}-\text{C})$. As a planar configuration at nitrogen could [if maintaining the value for $\angle(\text{Si}-\text{N}-\text{C})$] produce a C...C distance of 250 pm. Several refinements were carried out constraining the C_2NSi skeleton to be flat. The fit

became much poorer and some of the problems in fitting the 240–260 pm region were accounted for by adjustments of the Si–N and N–C bond lengths. The results of a refinement analogous to those of the previous study and of refinement I in this study are included in Table 2 [III]. The R_G/R_D values were 17.1/9.9 %. With the exception of $u(\text{N}\cdots\text{H}(\text{methyl}))$ all the refined u -values were smaller for the planar than for the nonplanar model. Subsequent attempts to refine the planar model further resulted in highly unreasonable nonbonded amplitudes and poorer fits to the data than their nonplanar counterparts.

The weighted difference curves for the combined molecular-scattering intensities and the difference radial-distribution curves are shown in Figs. 1(a) and 2(a), respectively, for the three sets of results (I, II, III) presented in Table 2. Set II is believed to give the best representation of

Table 5. Interatomic distances (r_a , pm) and amplitudes (u , pm) for $\text{SiH}_3\text{N}(\text{CH}_3)_2$; refinement II, Table 2.^a

	Distances	Amplitudes	
C–H	111.8(6)	7.5(5)	u_1
Si–H	146.6(19)	8.8(tied to u_3)	
N–C	145.7(6)	4.8(3)	u_3
N–Si	171.3(5)	4.9(3)	u_4
H \cdots H	181.3(18)	11.0(fixed)	
H \cdots H	242.6(63)	12.0(fixed)	
N \cdots H	212.5(15)	11.3(10)	u_7
N \cdots H	256.3(42)	10.5(tied to u_9)	
C \cdots C	241.6(11)	5.8(12)	u_9
C \cdots Si	276.1(6)	7.4(3)	u_{10}
C \cdots H	261.1(123)	20.0(fixed)	
C \cdots H	277.7(144)	20.0(fixed)	
C \cdots H	338.2(27)	15.0(fixed)	
Si \cdots H	368.2(43)	20.0(fixed)	
Si \cdots H	287.7(93)		
Si \cdots H	320.7(140)		
Si \cdots H	337.7(130)		
Si \cdots H	278.6(57)		
Si \cdots H	359.8(94)		
C \cdots H	331.8(63)	20.0(fixed)	
C \cdots H	307.0(64)		
C \cdots H	391.0(38)		

^a The other H \cdots H non-bonded distances were included in the refinement, but are not listed here.

the molecular structure of silyldimethylamine. The full list of interatomic distances and amplitude values is given in Table 5, and Table 8 contains the least-squares correlation matrix.

b. (Methylsilyl)dimethylamine (MH2). The appearance of the radial-distribution curve for MH2 [Fig. 2(b)] is similar to that of MH3, but all the bond distance peaks are now composite (see Table 6): There are two types of C–H bonds [C(N)–H and C(Si)–H] at 110 pm which were assumed to be of equal length, Si–H and C–N both contribute to the peak at 145 pm, but the contribution from $r(\text{Si–H})$ is even less than in MH3, making its determination even more difficult, and this was further complicated by new overlap problems in the region of the one-angle distances involving the silyl hydrogens. Finally, the Si–N and Si–C bond distances overlap to give a skewed peak with a maximum at 175 pm.

The Si \cdots C distance is the major component of the pronounced peak at 275 pm. The region between 200 and 275 pm includes contributions from the C \cdots C distance of the dimethylamino group, the Si \cdots H (methyl), N \cdots H (methyl) and N \cdots H (silyl) distances as well as some two-angle distances, but in the radial-distribution curve the only clear feature is a shoulder at *ca.* 245 pm. All parameters relating to the silyl hydrogen atoms had to be assumed and there was also some difficulty in assessing the C \cdots C distance, on which $\angle(\text{C–N–C})$ and $\angle(\text{N–Si–C})$ depend as the three Si \cdots H distances in the Si–CH₃ group are very close indeed. The remaining skeletal one-angle distance, N \cdots C is located at about 290–300 pm, *i.e.* at the trailing end of the peak at 275 pm.

Beyond 275 pm there are several contributions from C \cdots H, N \cdots H and Si \cdots H distances, the locations of which depend heavily on the torsional parameters of the methyl groups [θ_1 , θ_2 , θ_3 , see previous section]. Several refinements involving these parameters were carried out in course of the analysis, but in the end it was found that they all appeared to be close to staggered [$\theta=60^\circ$] and they were maintained in such orientations in the final refinement.

The overall conformation of the molecule is determined by the location of two long C \cdots C distances. For a pyramidal –N(CH₃)₂ group these C \cdots C distances varied in the range 320 to 435 pm for $\phi(\text{Si–N})$ values of 0° [both equal to 366 pm] to 180° [both 395 pm] the extreme values

being found for $\phi=75^\circ$ [320 pm] and $\phi=100^\circ$ [435 pm].

Comparisons of the radial-distribution curves for MH3 and MH2 [Figs. 2(a) and (b), respectively] suggest that the C...C distance may be about 420 pm and 375 pm. However, it should be remembered that a large number of distances involving the methyl hydrogen atoms [N...H, C...H, Si...H] also contribute to the area beyond 275 pm and so great care is needed. Refinements were therefore carried out for $\phi(\text{Si}-\text{N})$ in the range $0-180^\circ$ in intervals of 15° [assuming $\theta_1=\theta_2=\theta_3=60^\circ$ and $\angle(\text{SiCH})=\angle(\text{NHC})=109^\circ$]. A pronounced minimum in the least-squares fit [R_G] was obtained for $\phi=150^\circ$ and slight minima were located at 20° and at 90° . In a later test the two latter coincided, giving a broad shallow minimum at 70° [*maxima* at 10 and 120°], and the most favoured angle was 160° . The preferred conformation [$\phi=150^\circ$, in the final refinement] has a $\theta(\text{C}-\text{N}-\text{Si}-\text{C})$ value of about 70° , and it is similar to the conformation of ethyldimethylamine, which has $\theta(\text{C}-\text{N}-\text{C}-\text{C})=74(4)^\circ$ in gas-phase.¹³

It should be mentioned that the refinements were somewhat hampered by difficulties in obtaining consistent improvements in the least-squares fit to both sets of data. Often a good overall fit was obtained at the expense of poor fit to the short camera data. Refinements based on the latter only gave R_G/R_D values of 9.71/12.85 %. The results of a subsequent refinement based on both data sets are presented in Table 3. The R_G/R_D values were 11.4/13.7 % (short), 10.1/6.6 % (long) and 10.7/8.1 % (overall). In further refinement in which $\angle(\text{N}-\text{C}-\text{H})$ and $\angle(\text{Si}-\text{C}-\text{H})$ were 112° the agreement factors of 15.0/15.5 (short), 4.8/4.6 % (long) and 7.5/7.3 % (overall). However, in none of these refinements did parameter values change by more than one standard deviation from those obtained in the short-camera refinement. We have chosen to present our final results in terms of those given in Table 3, although there were refinements that gave better *overall* agreement factors. Corresponding interatomic distances and amplitude values are given in Table 6, and Table 9 contains the correlation matrix. The weighted difference curve for the combined molecular scattering intensities and the difference radial-distribution curve are shown in Figs. 1 (b) and 2 (b), respectively.

Table 6. Interatomic distances (r_a , pm) and amplitudes (u , pm) for $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$.^a

Distances		Amplitudes	
Torsion independent			
C-H	111.6(4)	7.5(5)	u_1
Si-H	148.5(fixed)	8.4(fixed)	
N-C	145.5(3)	4.4(5)	u_3
N-Si	171.5(6)	5.2(5)	u_4
Si-C	186.7(6)	5.5(tied to u_4)	
H...H	177.3(35)	11.0(fixed)	
H...H	177.4(42)	12.0(fixed)	
N...H	215.7(26)	14.7(fixed)	
Si...H	252.7(42)	11.5(fixed)	
N...H	260.5(13)	12.0(fixed)	
C...H	273.4(15)	12.0(fixed)	
C...C	242.2(12)	5.2(12)	u_{12}
C...Si	276.9(1)	8.3(5)	u_{13}
N...C	299.4(50)	10.9(24)	u_{14}
C...H	274.3(47)	18.0(fixed)	
C...H	341.3(25)		
Si...H	366.0(28)		
Si...H	287.1(43)		
Si...H	336.9(45)	20.0(fixed)	
N...H	329.4(87)		
N...H	396.1(53)		
Torsion dependent ^a			
C...C	367.7(65)	19.0(45)	u_{22}
C...C	420.7(34)	19.4(45)	u_{23}
C...H	395.3(11)	20.0(fixed)	
C...H	315.1(25)		
C...H	296.9(13)		
C...H	363.3(34)		

^a The other non-bonded H...H distances and the twelve torsion dependent C...H distances [$u=22$ pm] were included in the refinement, but are not listed here.

It is noteworthy that in the refinements carried out to find the preferred conformation there were substantial variations in the refined parameter values: $\angle(\text{Si}-\text{N}-\text{C})$, $119-122^\circ$; $\angle(\text{C}-\text{N}-\text{C})$, $109-115^\circ$; and $\angle(\text{N}-\text{Si}-\text{C})$, $105-116^\circ$. Refinements were therefore also carried out with the SiNC_2 skeleton constrained to be planar [$\alpha=360^\circ$] and the fit to the data was similar to that obtained for the nonplanar model. Changes in the skeletal bond distances were insignificant, and the $\text{Si}-\text{N}-\text{C}$ angle remained unaltered [$121.5(5)^\circ$], but the $\angle(\text{C}-\text{N}-\text{C})$ therefore increased to 116.8° . The $\text{Si}-\text{C}-\text{H}$ angles refined to $105.5(35)^\circ$

thus giving reversed relative magnitudes for C...C and Si...H which were now 247 and 244 pm. The N-Si-C angle did not change, but some amplitude values were larger than their counterparts in the nonplanar model [$u_{12}=7.5(24)$, $u_{14}=13.3(35)$, $u_{22}=32.6(10)$, and $u_{23}=24.0(60)$ pm]. The torsional angle was $\phi(\text{Si-N})=143(3)^\circ$ thus giving the C...C distances which depend on conformation (d_{22} and d_{23}) values of 350 and 416 pm.

It is believed that comparisons of the refinements of the two models support the nonplanar model, and that the fit represented by the planar model is an artifact due to the unfortunate distance overlap of C...C and Si...H (methyl). In MH3 (which has no Si...H (methyl) distances) the attempts to fit the planar model did not change the C...C distances significantly.

c. (Dimethylsilyl)dimethylamine (MH1). The interpretation of the radial-distribution curve [Fig. 2(c)] in terms of the interatomic distances [Table 7] is similar to that for the previous two molecules. Parameters relating to the silyl hydrogen atom [H1, Figs. 3 and 4], which contributes little to the total scattering, were fixed at assumed values [Table 4]. The maximum for the composite Si-N/Si-C peak is shifted up to 183 pm reflecting the larger contribution of $r(\text{Si-C})$. The area preceding the large peak at 275 pm is now dominated by the one-angle Si...H distances and the contribution from the one C...C one-angle distance is thus even more difficult to locate. The maximum at 275 pm coincides with those for the previous molecules, suggesting Si...C one-angle distances of rather similar lengths in the three molecules. The distinct shoulder above this peak contains contributions from N(Si)C [doubled in weight relative to MH2] and C(Si)C one-angle distances. There are also more C...H and N...H contributions to the area beyond 270 pm than there were for MH3, and these tend to obscure the locations of the four C...C distances which determine the overall conformation of MH1. There are significant features in the radial-distribution curve at about 420 and 370 pm [as for MH2] and around 330 pm. [Figs. 2 (a), (b) and (c)]. However, bearing in mind the complications caused by the many Si...H, N...H and C...H distances, a search was carried out to find the conformer(s) with the best fit to the data by varying $\phi(\text{Si-N})$ over the range of 0 to 180° in increments of 5° . There were

pronounced minima at about 35, 90–105 and 135° and the background correction was optimized for each of these three conformers. The structures obtained in these refinements had overall R_G -values of 16.5 % for $\phi=34(5)^\circ$, 14.5 % for $\phi=98(3)^\circ$, and 18.2 % for $\phi=145(3)^\circ$. In these three structures the conformation-dependent C...C distances were 363, 426, 409 and 308 pm; 421, 381, 351 and 334 pm; and finally 425, 330, 306 and 373 pm, respectively. Thus it seems that the first and third minima can be attributed to structures in which some C...C distances are fortuitously the same as those in the second conformation. This favoured conformer [$\phi=98^\circ$] has one Si-H bond nearly eclipsing one N-C bond, and in this respect it resembles the favoured conformer of MH2. However, the closest C-N-Si-C arrangements, of which there are now two, have approximate *gauche* conformations, with one N-CH₃ trapped within the Si(CH₃)₂ group [See Fig. 4]. Attempts were also made to interpret the data in terms of a mixture of two conformers, but no improvement in the fit to the data was obtained.

It should be noted that if all four methyl torsion angles were treated as independent parameters, all three conformations gave good fits to the data, with R_G ca. 11 %. It seems that almost the whole curve in the region beyond 270 pm could be fitted by the many C...H, N...H and Si...H distances, if the system was given enough degrees of freedom. In these refinements the main parameters varied very little, values in the ranges of $109-111^\circ$, $109-111^\circ$, $119.5-120.5^\circ$ and $111-112^\circ$ being obtained for the N-Si-C, C-Si-C, Si-N-C and C-N-C angles, respectively while $\angle(\text{Si-C-H})$ was fixed at 109.5° . The u -values for the bonded distances emerged large in all cases, particularly for the N-C bond which had an amplitude of about 5.9 pm.

All things considered it seems that the *gauche* form is the most probable conformer. This structure was refined further maintaining staggered conformations for the N-methyl groups [$\theta_1=\theta_2=60^\circ$, a_4 in Table 4] and C_2 symmetry for the Si(CH₃)₂ group. The results of the final refinement are given in Table 4, and corresponding interatomic distances and amplitude values are given in Table 7; Table 10 contains elements of the least-squares correlation matrix. The R_G/R_D values were 10.10/9.80 (short), 7.58/5.50 (long) and 8.82/6.91 % (overall), and the weigh-

Table 7. Interatomic distances (r_a , pm) and amplitudes (u , pm) for $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$.

	Distances	Amplitudes	
Torsion independent			
C-H	111.5(4)	8.5(3)	u_1
Si-H	148.5(fixed)	8.4(fixed)	
N-C	146.0(4)	6.7(3)	u_3
N-Si	171.9(5)	5.9(tied to u_5)	
Si-C	186.9(3)	6.2(3)	u_5
H...H	179.7(6)	11.0(fixed)	
H...H	184.1(23)	12.0(fixed)	
N...H	213.7(5)	12.0(fixed)	
Si...H	244.8(32)	12.0(7)	u_9
N...H	262.0(5)	11.0(fixed)	
C...H	275.7(18)	11.0(fixed)	
C...C	244.5(23)	6.0(tied to u_9)	
C...Si	274.6(12)	9.2(6)	u_{13}
C...C	301.4(77)	10.6(20)	u_{14}
N...C	293.8(36)	10.6(tied to u_{14})	
C...H	274.0(26)	18.0(fixed)	
C...H	341.6(18)		
Si...H	325.9(33)		
Si...H	282.7(18)		
Si...H	365.8(14)		
C...H	299.1(90)		
C...H	338.9(138)	20.0(fixed)	
C...H	393.2(52)		
N...H	383.2(48)		
N...H	296.2(85)		
N...H	333.5(73)		
N...H	332.7(89)		
N...H	383.5(40)		
N...H	296.8(75)		
Torsion dependent ^a			
C...C	421.6(40)	15.0(fixed)	
C...C	383.5(82)	20.0(fixed)	
C...C	352.8(82)	23.0(fixed)	
C...C	335.4(60)	23.0(fixed)	
C...H	298.1(18)	20.0(fixed)	
C...H	395.9(10)	20.0(fixed)	

^a The other H...H and the 24 torsional dependent C...H distances [$u=22$ pm] were included in the refinement, but are not listed here.

ted difference curve for the combined molecular scattering intensities and the difference radial-distribution curve are shown in Figs. 1(c) and 2(c), respectively.

The C-Si-C angle is rather narrow, but it refined consistently to this value [107.6(20)°] for

several sets of refinements with different starting values for the parameters and constraints with respect to u -values. Introduction of deviation from C_s symmetry for N-SiHC₂ did not lead to an improved fit to the data nor to significant distortion from this symmetry although it appeared that $\angle(\text{N-Si-C3})$ was consistently larger than $\angle(\text{N-Si-C4})$: 110.9(20) and 108.6(24)°, respectively with a corresponding value of 107.4° for $\angle(\text{C-Si-C})$.

A search for the best conformer with a planar configuration at nitrogen was also carried out and minima were obtained for $\phi=40$ and 70, 85°, but in each case the pyramidal form was favoured over the planar one. Finally, planarity was imposed on the refined *gauche* conformation [Table 4], and it refined consistently through various routes to a structure which had $\phi(\text{Si-N})=135(5)^\circ$ and R_G/R_D values of 12.95/11.41 (short); 8.95/5.96 (long) and 11.05/7.75 % (overall). The skeletal bonded distances were slightly shorter than in the nonplanar structure and both the N-Si-C and C-Si-C angles were about 111.5°. The overall distortion of the skeleton was such as to give quite similar conformation-dependent C...C distances [432, 364, 324 and 398 pm] as those of the nonplanar form [Table 7].

DISCUSSION

Perspective views of $\text{SiH}_3\text{N}(\text{CH}_3)_2$, $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$ and $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$, corresponding to the final molecular structures as given in Tables 2 (II), 3 and 4 respectively, are presented in Fig. 3. However, comparisons of the rotamer preferences are best understood in terms of projections along the Si-N bonds as shown in Fig. 4. It is seen that the preferred conformations of MH2 and MH1 [Figs. 4(b) and (c), respectively] are basically twisted some 30° from the position which has perfect staggering of (H/R)₃Si-NR₂E where E denotes the lone electron-pair on nitrogen. This staggered conformation was assumed for $\text{SiH}_3\text{N}(\text{CH}_3)_2$ [Fig. 4(a)], but there was a marginal indicated preference for a ϕ -angle of 15° for this compound, corresponding to a conformation that approaches those of MH2 and MH1. Other conformers considered for MH2 and MH1 also had this basic feature, but they differed in relative positions of methyl groups

Table 8. Least-squares correlation matrix ($\rho_{ij} \times 100$) for $\text{SiH}_3\text{N}(\text{CH}_3)_2$. Only elements $|\rho| \geq 50$ are listed.

	r_3	r_4	a_1	a_5	u_3	u_4	u_7	u_9	u_{10}	k_1	k_2
r_2	-92	68		-50							
r_3		-59	-53								
a_3					-56			-50		-56	-58
a_4				51							
a_5							58	-60			
u_3						57			65	89	
u_4										67	
u_8										72	

and hydrogen atoms with respect to the $\text{N}(\text{CH}_3)_2$ framework. Ultimately the conformations which had near *syn* conformations of $\text{C}_2\text{-N-Si-H}_1$ were preferred over those which had nearly eclipsed N-C and Si-C bonds. The closest C-N-Si-H angles were 12 and 24° whereas the

Table 9. Least-squares correlation matrix ($\rho_{ij} \times 100$) for $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$. Only elements $|\rho| \geq 50$ are listed.

	r_5	a_3	a_5	a_7	u_3	u_{12}	k_1
r_1							56
r_4	68	76					
r_5		74					
a_1			84	50			
a_2		58					
a_5				60			
a_7						-62	
u_1					62		76
u_3							79

Table 10. Least-squares correlation matrix ($\rho_{ij} \times 100$) for $(\text{CH}_3)_2\text{SiHN}(\text{CH}_3)_2$. Only Elements $|\rho| \geq 50$ are listed.

	a_2	a_5	a_6	a_8	a_9	a_{10}	u_{14}	k_1	k_2
a_1	-52	54		68		-60			
a_2				-86		63			
a_5			-87				78		
a_6					52		-84		
a_8						-62			-50
a_9						-68			
u_1								72	50
u_4								64	
u_{11}							54		
k_1									57

close C-N-Si-C angles were in the range 50–72° [Fig. 4].

In MH2 [$\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$] the preferred conformation has Si-CH_3 in a *gauche* conformation with respect to the lone-pair on nitrogen rather than *anti*. This is consistent with the situation for $\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)_2$, as shown by gas-phase infrared and Raman spectra¹⁴ and confirmed by an electron-diffraction study.¹³ Comparable angles are $\theta(\text{C-C-N-C})=74(4)^\circ$ (which corresponds to $\theta(\text{C-C-N-E})=47^\circ$) for $\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)_2$ and $\theta(\text{C-Si-N-C})=72(3)^\circ$ (equivalent to $\theta(\text{C-Si-N-E})=30^\circ$) for $\text{CH}_3\text{SiH}_2\text{N}(\text{CH}_3)_2$. It appears that such *gauche* arrangements also govern the conformational preferences in other enthylamines,^{14,15} although triethylamine is said to be in an AGG' conformation (C_s -symmetry) in the gas-phase.¹⁶

The structures of the dimethylamino groups in the present series of silyl methylamines are similar to those of $\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)_2$,¹³ $\text{N}(\text{CH}_3)_3$ ¹⁷ and $\text{HN}(\text{CH}_3)_2$ ¹⁷ in which C-N-C angles are 111.3(10), 110.6(6) and 111.8(6)°, respectively and $r_a(\text{N-C})$ are 145.2(6), 145.4(2) and 145.5(2) pm, although the r -value for $\text{N}(\text{CH}_3)_3$ has been corrected to $r_g=146.1$ pm [*i.e.* $r_a=145.9$ pm] in a reanalysis based on electron-diffraction and spectroscopic data in combination.¹² Thus, the shallow pyramidal configuration at nitrogen in the silylamines is mainly a consequence of the wide Si-N-C angles [about 120°, Tables 2 to 4] which, it may be argued, are a result of non-bonded repulsions as the preferred one-angle $\text{Si}\cdots\text{C}$ distance should be 280 pm [non-bonded radii¹⁸ are 125 pm (C) and 155 pm (Si)] as compared to values of 276.1(6), 276.9(10) and 274.6(12) pm obtained for MH3, MH2 and MH1, respectively. It should be noted that there is a gradual widening of the C-N-C angle through

this series of compounds: 112.0(6), 112.7(8) and 113.7(15) $^\circ$ giving C...C one-angle distances of 241.6(11), 242.2(12) and 244.5(23) pm and that all these distances and angles are slightly greater than those in HN(CH₃)₂,¹⁷ N(CH₃)₃^{12,17} and CH₃CH₂N(CH₃)₂.¹³

It has been suggested¹⁹ that in (CH₃)₃CN(CH₃)₂ there is a common potential surface for *t*-butyl rotation and nitrogen inversion. It is interesting that the structures obtained for the present methylsilyldimethylamines are intermediate to the proposed minimum-energy and transition-state structure of the trialkylamine which have a pyramidal nitrogen with staggered conformation and planar nitrogen with one eclipsed C-CH₃ and N-CH₃ pair, respectively.

It should be noted that in the present investigation [as in the investigation of CH₃CH₂N(CH₃)₂, N(CH₃)₃ and HN(CH₃)₂ in Refs. 13 and 17] no shrinkage corrections have been applied. Thus the structure obtained do not represent the equilibrium with respect to either rotation about the N-Si bond or inversion about nitrogen. In view of the results for the trialkylamines the dynamics of these two motions should be considered together. However, at the present stage the question of pyramidal or planar configuration at nitrogen requires comment. The preferences for pyramidal structures were not as clear for MH1 and MH2 as for MH3 [Table 2]. However, planar equilibrium structures are possible for all three molecules with the observed non-planarity being purely a shrinkage effect. In any case the pyramids are rather shallow. Thus the structures of all the dimethyl(silyl)amines are intermediate between those of the pyramidal trimethylamine, and the truly planar methylsilylamines.^{20,21}

The effect of methylsubstitution on the Si-N bond lengths is insignificant [171.3(5), 171.5(6) and 171.9(5) pm, Tables 2 to 4], but permethylation may result in a significant lengthening as indicated by the results for (H₃Si)₂NH [172.5(3) pm]²² and [(CH₃)₂Si]₂NH [173.8(5) pm]²³ and for (H₃Si)₃N [173.4(2) pm]²⁴ and [(CH₃)₃Si]₃N [175.9(3) pm].²⁵ However, in all these dimethyl(silyl)amines the Si-N bonds are short, and this has been taken as evidence for pπ-dπ bonding. Regardless of the origin of the flattening of the pyramidal configuration in silylamines, it is possible that as the Si...C distance increases, the availability of the lone-pair of nitrogen for such

π-bonding may increase and this could lead to bond shortening. Other parameters [angles N-Si-C and C-Si-C and Si-C bond lengths] are unexceptional.

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