Determination of the Molecular Structures and Conformations of Methylbis(methylsilyl)amine and Bis(dimethylsilyl)methylamine in the Gas Phase by Electron Diffraction

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The molecular structures of methylbis(methylsilyl)amine, $NMe(SiH_2Me)_2$, and bis(dimethylsilyl)-methylamine, $NMe(SiHMe_2)_2$, in the gas phase have been determined by electron diffraction. In both molecules the $NCSi_2$ skeleton is planar. Principal parameters (r_a) for $NMe(SiH_2Me)_2$ are: r(Si–N) 171.8(3), r(Si–C) 186.4(5), r(C–N) 149.2(12) pm; Si–N–Si 125.6(10) and N–Si–C 113.5(18)° and for $NMe(SiHMe_2)_2$ are: r(Si–N) 172.7(4), r(Si–C) 187.2(3), r(C–N) 148.3(7) pm; Si–N–Si 126.1(5), N–Si–C 110.8(5), and C–Si–C 115.5(10)°. In $NMe(SiH_2Me)_2$ the SiH_2Me groups are twisted about 60 and 120° from the positions in which the Si–C bonds eclipse the N–C bond, so that the methyl groups are mutually *trans* when viewed along the Si ••• Si axis. In $NMe(SiHMe_2)_2$ the $SiHMe_2$ groups are twisted 20 and 120° from positions in which the Si–H bonds are *trans* to the N–C bond.

It has long been known that the NSi_3 skeletons of trisilylamines are planar, in gas [1–3] and solid phases,[4] whereas trialkylamines are pyramidal,[5] although the reasons for this difference have been debated inconclusively. Amines with one silyl and two methyl substituents are shallow pyramids, with CNC angles around 112° and SiNC angles around 120°, when the silyl groups are SiH_3,[6,7] SiH_2Me, or $SiHMe_2$,[7] but planar when the silyl group is $SiMe_3$.[8] It is not clear whether the apparent shallow pyramids arise from shrinkage effects, with planar average geometry and large-amplitude out-of-plane deformations, but it is clear that in this group of molecules the potential functions for these vibrations must be very shallow, wherever the minima are. Only one structure has been reported[9] for an amine with one methyl and two silyl substituents, namely $NMe(SiH_3)_2$, and in this the skeleton is planar. It is therefore of interest to know whether this is always so, or whether non-planarity may be induced by introducing ligands of low symmetry. We have therefore determined the structures of $NMe(SiH_2Me)_2$ and $NMe(SiHMe_2)_2$. The conformations of these compounds are also important. It has been noted that the conformations adopted by $O(SiMe_3)_2$ [10,11] and $NH(SiMe_3)_2$ [12] are extremely similar, as are those of $O(SiHMe_2)_2$ [13] and $NH(SiHMe_2)_2$.[14] The implication of these observations is that 1,3-interactions are more important in determining conformational preferences. Our studies enable us to see whether this is still true when the central nitrogen atom has a methyl substituent instead of hydrogen.

Experimental

Samples of $NMe(SiH_2Me)_2$ and $NMe(SiHMe_2)_2$ were prepared by gas-phase reactions of the appropriate chlorosilanes with NH_2Me, and purified by fractional condensation *in vacuo*. Purities were checked by i.r. and n.m.r. spectroscopy.

Electron-diffraction scattering intensities were recorded on Kodak Electron Image plates, using the Edinburgh diffraction apparatus,[15,16] with nozzle-to-plate distances of 128 and 286 mm and an accelerating voltage of *ca.* 44 kV. During exposures the nozzle was maintained at 295 K, and the samples at 295 K [$NMe(SiHMe_2)_2$] or 273 K [$NMe(SiH_2Me)_2$]. Data were obtained in digital form using a computer-controlled Joyce-Loebl Microdensitometer 6, with automatic plate-centring, and the scanning program described previously.[17] 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-reduction[17] and least-squares refinement programs.[18] Weighting points used in setting up the off-diagonal weight matrices are given in Table 1, with other relevant data. In all calculations the complex scattering factors of Schäfer *et al.*[19] were used.

Results

Molecular Models.—The geometries of the molecules were described by the parameters listed in Table 2. In each case the two halves of the molecule were taken to be identical and to have local C_s symmetry, except with regard to the twist angles of the various groups. Planarity at nitrogen was assumed in the $NMe(SiHMe_2)_2$ model but not in the case of $NMe(SiH_2Me)_2$. However, for $NMe(SiH_2Me)_2$, the $NCSi_2$ skeleton remained very close to planar at all stages and latterly planarity was imposed. The angles at silicon in the $NSiH_2Me$ groups were

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

Compound	Camera height/ mm	Wavelength/ pm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor
			nm^{-1}						
$NMe(SiH_2Me)_2$	128.3	5.682	4	60	70	300	324	0.055	0.939(20)
	285.7	5.681	2	20	50	120	140	0.064	0.913(11)
$NMe(SiHMe_2)_2$	128.3	5.700	4	60	80	300	340	0.182	0.835(19)
	285.8	5.700	2	20	40	120	144	0.270	0.837(10)

Table 2. Molecular parameters[a]

	$NMe(SiH_2Me)_2$	$NMe(SiHMe_2)_2$
Independent distances/pm		
r_1(C-H)	112.0(6)	111.8(5)
r_2(C-N)	149.2(12)	148.3(7)
r_3(Si-H)	147.6(16)	149.0 (fixed)
r_4(Si-C)	186.4(5)	187.2(3)
r_5(Si-N)	171.8(3)	172.7(4)
Independent angles/°		
a_1(N-C-H)	108.0 (fixed)	110.0 (fixed)
a_2(Si-C-H)	111.2(10)	108.8(8)
a_3(N-Me twist)[b]	−30.0 (fixed)	0.0 (fixed)
a_4(Si-N-Si)	125.6(10)	126.1(5)
a_5(N-Si-C)	113.5(18)	110.8(5)
a_6(Si-N twist)[b]	54.5(18)	121.4(41)
a_7(Si-N twist)[b]	123.0(29)	20.6(19)
a_8(Si-Me twist)[b]	60.0 (fixed)	0.0 (fixed)
a_9(H-Si-H)	109.0 (fixed)	
(C-Si-C)		115.5(10)
a_{10}(SiH_2 tilt)[b]	−4.0 (fixed)	
(N-Si-H)		109.5 (fixed)
Dependent angles/°		
a_{11}(Si-N-C)	117.2(6)	116.9(3)
a_{12}(N-Si-H)	106.5(5)	

[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] For definition, see text.

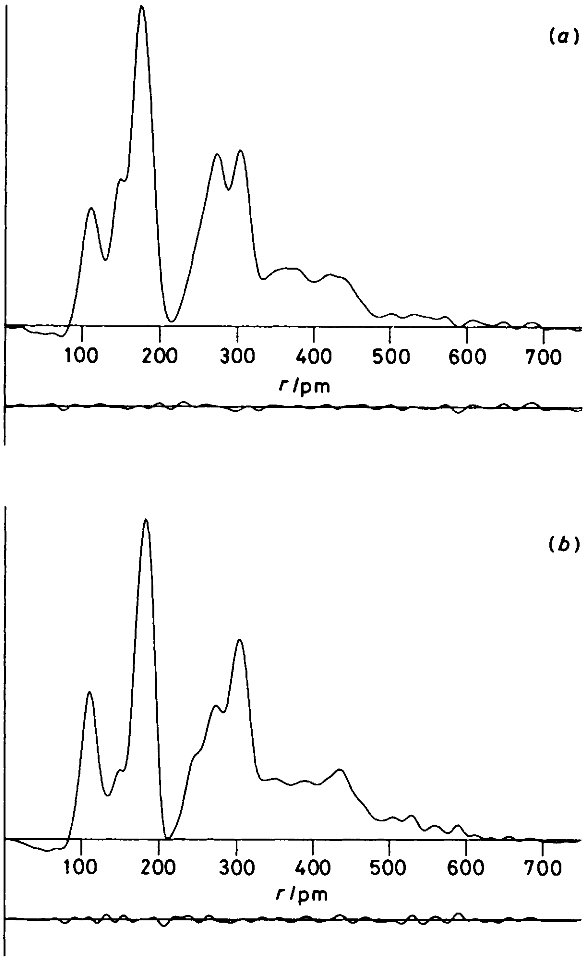

Figure 1. Experimental and final difference radial-distribution curves $P(r)/r$, for (*a*) $NMe(SiH_2Me)_2$ and (*b*) $NMe(SiHMe_2)_2$. In each case, before Fourier transformation, the data were multiplied by $s \cdot \exp[(-0.000\,02\,s^2)/(Z_{Si} - f_{Si})(Z_C - f_C)]$

defined by angles NSiC, HSiH, and a tilt of the HSiH plane so that the NSiC and HSiH bisectors no longer coincided. A positive tilt made the angle CSiH greater than NSiH. For the $NSiHMe_2$ groups the silicon angles were defined by NSiC, CSiC, and NSiH.

The overall conformations adopted by the molecules were described in terms of dihedral angles (θ) involving the unique silicon substituents, *i.e.* C–Si–N–Si for $NMe(SiH_2Me)_2$ and H–Si–N–Si for $NMe(SiHMe_2)_2$. In each case the *syn* arrangement was taken as the origin. The two twist angles could be constrained, for example, to be equal (giving overall C_2 symmetry) or equal and opposite (overall C_s symmetry) or to differ by a fixed amount, but these constraints were not used in the later stages of the work.

The N–Me and Si–Me groups were all assumed to have local C_{3v} symmetry, and in each molecule all C–H bonds were considered to be equal in length. The conformations of the Si–Me groups were defined by twist angles, which were H–C–Si–N dihedral angles, while H–C–N–Si dihedral angles defined the N–Me conformations. None of these parameters was well determined by the data, and they were all set at values which gave the best fit, but the changes in fit were extremely marginal, and no significance should be attached to the quoted values.

Refinement of $NMe(SiH_2Me)_2$.—The radial distribution curve, Figure 1(*a*), shows just three peaks below 200 pm, corresponding to five distances, even with the assumptions already made. The C–H bonds contribute to the first peak, and their distance refined easily, as did those for the Si–C and Si–N bonds, which give rise to the biggest peak. But the two remaining distances, C–N and Si–H, were strongly correlated (as shown in the least-squares correlation matrix, Table 3), and the amplitude of vibration for Si–H had to be fixed. Even so, the refined C–N distance is unusually long, but not unreasonably so given its large standard deviation, and the value obtained for $NMe(SiHMe_2)_2$. The N(C)H distance gave a weak peak, masked by the much more intense peaks of Si–N and Si–C, and so the N–C–H angle could not be refined.

The next section of the curve, up to *ca.* 320 pm, has two clear maxima, and a shoulder at 250 pm. This shoulder is mainly due to the Si(C)H atom pairs, and so the Si–C–H angle refined easily. However, the two major peaks contain contributions from Si(N)Si, Si(N)C, and N(Si)C, and as the Si–N and Si–C distances are not well resolved, this led to correlation between the remaining valence angles, Si–N–Si and N–Si–C. Nevertheless, it was clear that the $NCSi_2$ skeleton was planar within experimental error. The remaining part of the radial distribution curve depends entirely on the conformations of the various groups. The largest contributions to this region are from two Si(NSi)C atom pairs, two C(NSi)C pairs, and one C(SiNSi)C pair, but the many pairs involving hydrogen provide a substantial part of the total intensity. We therefore studied systematically a wide range of possible conformations in which the two Si–N twist angles were constrained either to be equal, or constrained so that one angle was 60 or 180° greater than the other. The best-fitting structure found by this means was refined further, without the constraint, and led eventually to the parameters given in Table 2, and the interatomic distances listed in Table 4. The final *R* factor (R_G) was 0.06, but only a slightly higher value was obtained for a conformation in which one of

Table 3. Least-squares correlation matrices (× 100). Only elements ⩾50 are listed

(*a*) $NMe(SiH_2Me)_2$

	r_3	a_4	a_5	a_7	u_2	u_4	u_6	u_7	u_{14}	u_{15}	k_2
r_1	56										
r_2	−84	72	−50		−53		−59				
r_3		−51									
a_4			−93	59			−88				
a_5				−68			90			52	
a_7							−67		−58		
u_2						51					
u_{10}								61			
k_1											59

(*b*) $NMe(SiHMe_2)_2$

	a_4	a_5	a_9	u_4	u_{15}	k_1
r_5	−51					
a_2						−50
u_5				74		
u_6		73	−64			
u_{14}					63	
k_2				54		

Table 4. Interatomic distances (r_a/pm) and amplitudes of vibration (u/pm)[a]

	$NMe(SiH_2Me)_2$		$NMe(SiHMe_2)_2$	
	Distance	Amplitude	Distance	Amplitude
r_1(C–H)	112.0(6)	8.8(3)	111.8(5)	7.9(5)
r_2(C–N)	149.2(12)	4.9(3)	148.3(7)	4.5 (fixed)
r_3(Si–H)	147.6(16)	8.9 (tied to u_2)	149.0 (fixed)	8.5 (fixed)
r_4(Si–C)	186.4(5)	6.5(3)	187.2(3)	5.7(3)
r_5(Si–N)	171.8(3)	5.9 (tied to u_4)	172.7(4)	5.2(6)
r_6(Si ··· Si)	305.7(18)	9.5(9)	307.9(7)	6.2(13)
r_7(Si ··· C)	274.3(9)	8.0(4)	274.0(8)	7.2(5)
r_8(N ··· C)	299.8(33)	7.9 (tied to u_6)	296.4(8)	6.2 (tied to u_6)
r_9(C ··· C)			316.7(14)	6.2 (tied to u_6)
r_{10}[Si(C)H]	249.8(15)	10.8(9)	247.0(10)	11.1(8)
r_{11}[N(C)H]	212.5(11)	11.0 (fixed)	214.1(8)	12.0 (fixed)
r_{12}[N(Si)H]	256.3(16)	12.0 (fixed)	263.1(5)	12.0 (fixed)
r_{13}[C(Si)H]	275.4(15)	12.0 (fixed)	267.4(11)	12.0 (fixed)
Torsion-dependent distances				
r_{14}[Si(NSi)C]	441.2(20)	15.2(25)	412.7(18)	15.0(50)
r_{15}[Si(NSi)C]	375.4(35)	15.0(22)	448.7(16)	15.7(28)
r_{16}[Si(NSi)C]			343.4(14)	10.0 (fixed)[b]
r_{17}[Si(NSi)C]			439.7(25)	15.7 (tied to u_{15})
r_{18}[C(NSi)C]	414.8(31)	15.2 (tied to u_{14})	433.6(12)	15.0 (fixed)
r_{19}[C(NSi)C]	347.8(72)	15.0 (tied to u_{15})	341.4(32)	14.6 (fixed)[b]
r_{20}[C(NSi)C]			372.0(19)	14.6 (fixed)[b]
r_{21}[C(NSi)C]			330.0(22)	14.6 (fixed)[b]
r_{22}[C(SiNSi)C]	546.4(38)	29.6 (fixed)[b]	421.4(48)	20.0 (fixed)
r_{23}[C(SiNSi)C]			504.7(36)	16.9 (fixed)[b]
r_{24}[C(SiNSi)C]			579.0(19)	16.9 (fixed)[b]
r_{25}[C(SiNSi)C]			528.3(37)	16.9 (fixed)[b]

[a] Other Si ··· H, N ··· H, C ··· H, and H ··· H distances were included in the refinements, but are not listed here. [b] Obtained in previous refinements, but not included in final refinements.

the twist angles was of opposite sign. Such a conformation would have a similar Si ··· C and C ··· C distance distribution to the preferred one, except for the longest C ··· C distance. Similarly, a mixture of conformers with both angles 54 and both 123° would be expected to give a comparable distribution of distances.

The refined parameters and distances are given in Tables 2 and 4. Observed and final weighted difference combined molecular-scattering intensities are presented in Figure 2(*a*), and Figure 3 shows a perspective view of the molecule.

Refinement of $NMe(SiHMe_2)_2$.—The radial distribution curve, Figure 1(*b*), is broadly similar to that for $NMe(SiH_2Me)_2$, but with some marked differences in relative intensities of peaks. In the region corresponding to the bonded distances the peak at *ca.* 150 pm is very small, but still has C–N and Si–H

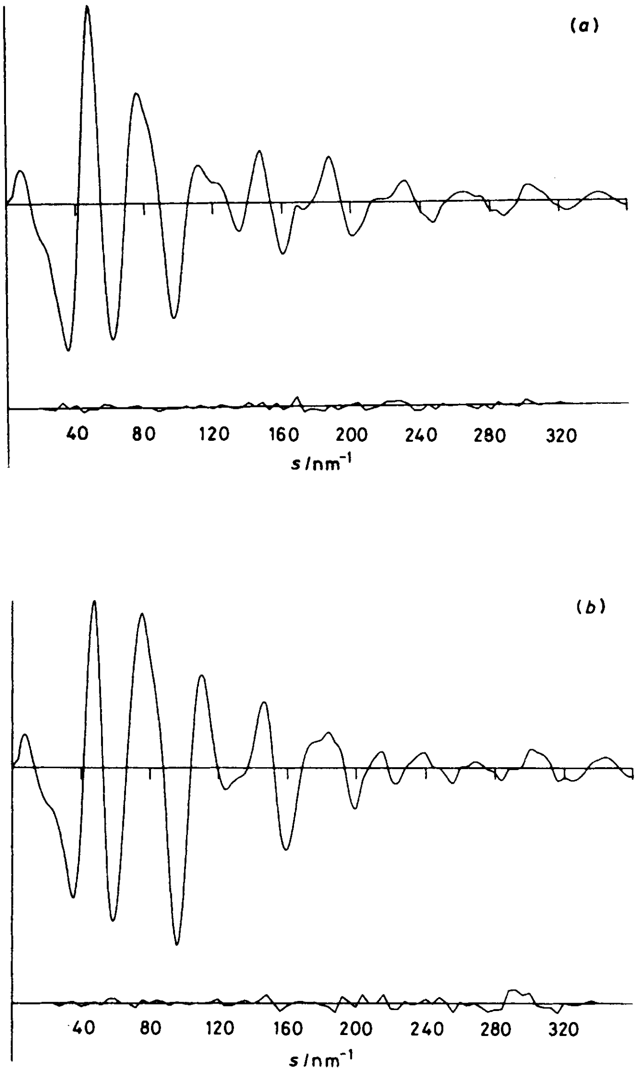

Figure 2. Observed and final weighted difference combined molecular-scattering intensity curves for (*a*) $NMe(SiH_2Me)_2$ and (*b*) $NMe(SiHMe_2)_2$

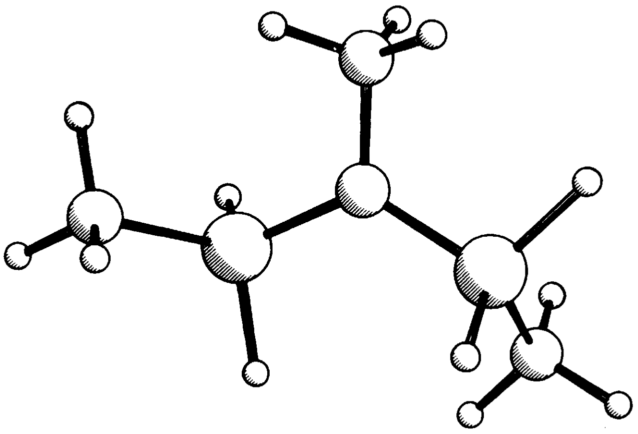

Figure 3. Perspective view of $NMe(SiH_2Me)_2$

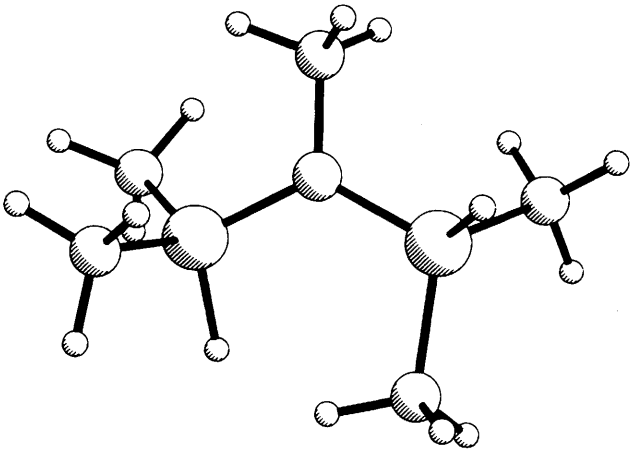

Figure 4. Perspective view of $NMe(SiHMe_2)_2$

contributions. It was necessary to fix the latter distance and both amplitudes of vibration. In the next region, the Si(C)H peak was clearly visible, but there were now three major components of the peak at *ca.* 300 pm *i.e*, Si(N)Si, N(Si)C, and C(Si)C. Consequently it was only possible to refine one amplitude of vibration for the group of three distances, and even then the angles Si–N–Si, N–Si–C, and C–Si–C were quite strongly correlated (Table 3).

The part of the radial distribution curve above 300 pm is very complicated, with 12 contributions from conformation-dependent Si $\cdots$ C and C $\cdots$ C distances, as well as myriads of distances involving hydrogen. We therefore systematically varied the two Si–N twist angles in steps of 15°, to cover all possibilities (well over 100). Six significant minima were found, with the angles *ca.* 15 and 15, 15 and −15, 105 and 105, 105 and −105, 120 and 15, and 120 and −15°. The fit to the data was best for the last two, and the difference radial distribution curves were also markedly better above 300 pm for these; hence the other four were rejected. A subsequent study of the remaining two conformations led to a significant preference for the form with angles having the same sign, and the angles eventually refined to 121(4) and 21(2)°, but it is conceivable that in the average structure the latter angle is close to zero and that there is a large amplitude torsional vibration leading to a shrinkage effect. In the last stages of the work various groups of vibrational amplitudes relating to the longer distances were allowed to refine, but in the final refinement, for which R_G was 0.08, most of these were fixed. Final parameters are given in Table 2 and interatomic distances in Table 4. Figure 2(*b*) shows the experimental and final difference molecular scattering curves, while Figure 4 shows a perspective view of the molecule.

Discussion

It is quite clear from these studies that the $NCSi_2$ skeletons of both molecules are planar, as is that of $NMe(SiH_3)_2$,[9] and that there is no large-amplitude out-of-plane vibration leading to a substantial shrinkage effect. Thus it seems that two silyl substituents on nitrogen are sufficient to ensure planarity, but that when there is one silyl substituent the energy difference between planar and pyramidal forms is small. Much has been said, inconclusively, about why these compounds have planar skeletons. One suggestion has been that non-bonded Si $\cdots$ Si interactions force the silyl groups apart, as the appropriate radius for silicon for one-angle contacts is 155 pm.[20] However, we find no marked evidence of steric effects. Table 5 shows that although the Si $\cdots$ Si distances are 300 pm in trisilylamines, they are 305—308 pm in the methylbis(silyl)amines, and 310 pm or more in disilylamines[12,21] (which have the widest SiNSi

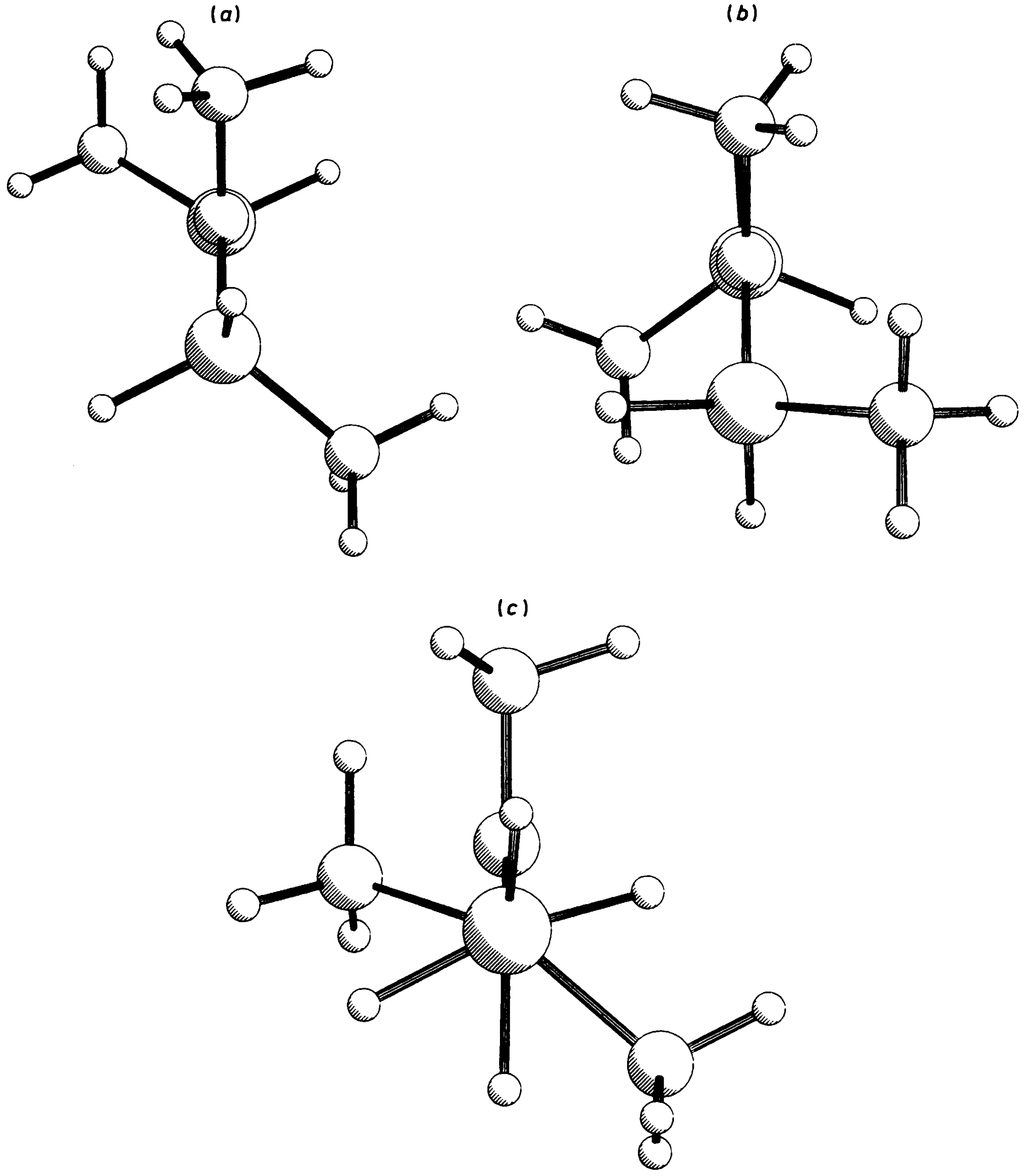

Figure 5. Conformation of $NMe(SiH_2Me)_2$, projections (*a*) and (*b*) along N–Si bonds and (*c*) along Si ··· Si (one Si atom is obscured by the other)

Table 5. Geometrical parameters, distances (pm) and angles (°), for some silylamines

Compound	Si–N	C–N	Si–C	Si ··· Si	Si ··· C	C ··· C	SiNSi	SiNC	CNC	NSiC	CSiC	Ref.
$N(SiH_2Me)_3$	172.9(13)		185.3(4)	299.5(6)			120.0			112.3(8)		3
$N(SiH_3)_3$	173.4(2)			299.7(3)			119.7(1)					2
$NH(SiMe_3)_2$	173.8(5)		187.6(1)	317(1)			131.3(15)			110.7(5)	108.3(5)	12
$NH(SiHMe_2)_2$	172.7(3)		186.7(3)	313.6(21)			130.4(15)			110.2(3)	112.8(11)	14
$NH(SiH_3)_2$	172.5(3)			309.7(6)			127.7(1)					21
$NMe(SiHMe_2)_2$	172.7(4)	148.3(7)	187.2(3)	307.9(7)	274.0(8)		126.1(5)	116.9(3)		110.8(5)	115.5(10)	
$NMe(SiH_2Me)_2$	171.8(3)	149.2(12)	186.4(5)	305.7(18)	274.3(9)		125.6(10)	117.2(6)		113.5(18)		
$NMe(SiH_3)_2$	172.6(3)	146.5(5)		306.8(6)	272.8(6)		125.4(4)	117.3(2)				9
$NMe_2(SiHMe_2)$	171.9(5)	146.0(4)	186.9(3)		274.6(12)	244.5(23)		119.3(8)	113.7(15)	109.9(18)	107.5(20)	7
$NMe_2(SiH_2Me)$	171.5(6)	145.5(3)	186.7(6)		276.9(10)	242.2(12)		121.5(8)	112.7(8)	113.3(23)		7
$NMe_2(SiH_3)$	171.4(4)	145.7(6)			276.1(6)	241.6(11)		120.9(3)	112.0(6)			7
NMe_3		145.9(2)				239.9(6)			110.9(6)			5

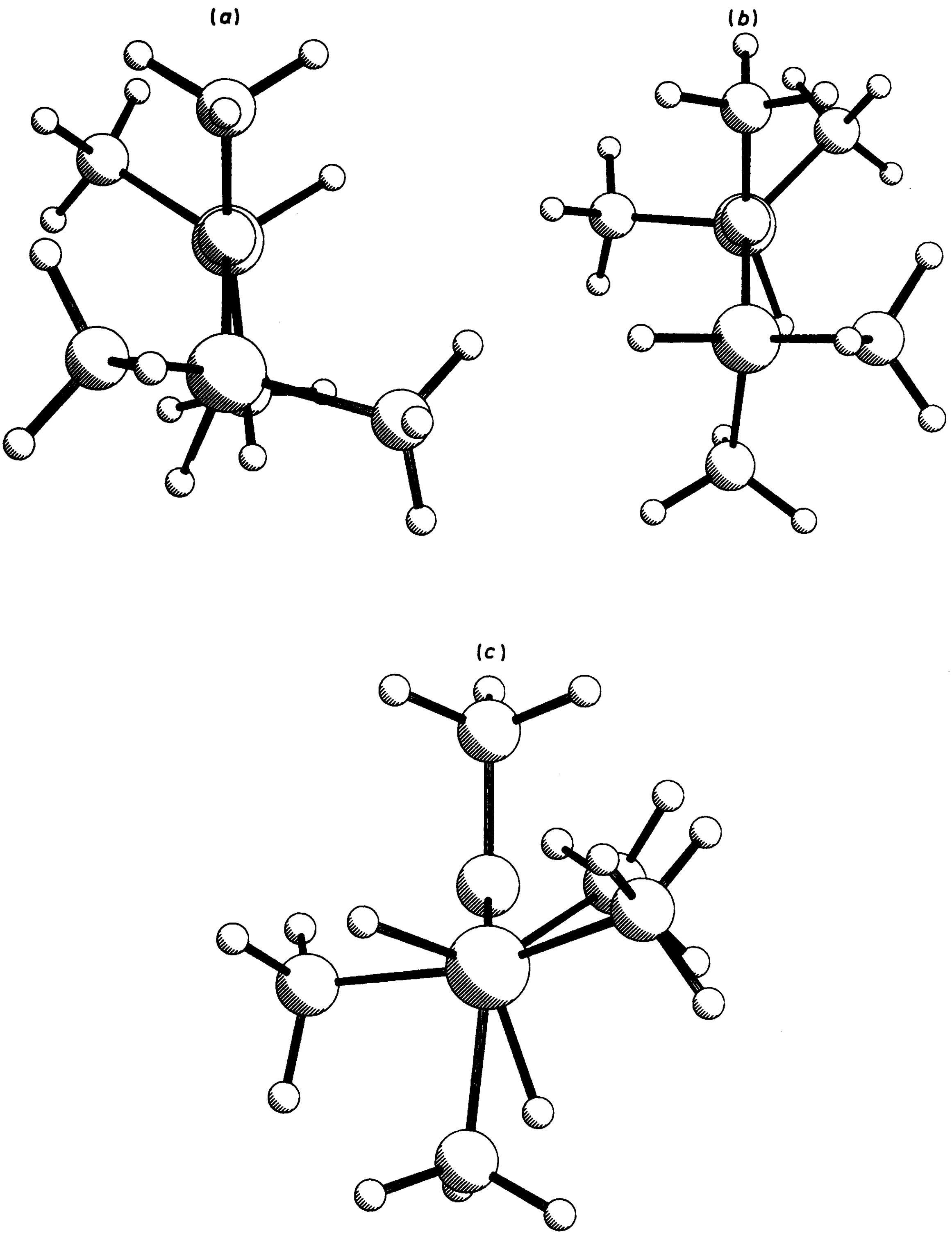

Figure 6. Conformation of $NMe(SiHMe_2)_2$, projections (*a*) and (*b*) along N–Si bonds, and (*c*) along Si ··· Si (one Si atom is obscured by the other)

angles), and so the distances are not close to their lower limit in these compounds. In contrast, the non-bonded Si ··· C and C ··· C distances shown in Table 5 are reasonably consistent, and it is noticeable that these distances vary much less than their associated bond angles, SiNC and CNC.

Bond lengths shown in Table 5 do not vary greatly. There is a small change in the Si–N distances, from 173 pm in trisilylamines to 172 pm in disilylamines and 171 pm in monosilylamines, and the C–N distances are somewhat longer in methylbis(silyl)amines than in dimethyl(silyl)amines. It may be significant that $NH(SiMe_3)_2$ has the longest Si–N and Si–C bonds and in this respect, studies of other amines with bulky trimethylsilyl substituents are important.

The remaining parameters listed in Table 5 relate to valence angles at silicon. These are clearly very variable, most markedly in the CSiC angles, with NSiC being 112—113° in the SiH_2Me

compounds, and otherwise 110—111°. This easy deformation of angles at silicon is widely observed, as for example in $PH_2[C(SiMe_3)_3]$, in which CSiC angles at one silicon atom range from 104 to 121°,[22] or in almost any crystallographic study of a trimethylsilyl compound where the individual angles are separately determined. There is, therefore, a possibility that there could be some variation of these angles within one compound: a possibility which we have not been able to investigate.

The conformations adopted by these amines, with regard to rotation about the Si–N bonds, are interesting. It has been noted that in $NH(SiMe_3)_2$[12] and $O(SiMe_3)_2$,[10,11] and in $NH(SiHMe_2)_2$[14] and $O(SiHMe_2)_2$,[13] there is great similarity of preferred conformations, and it has been suggested that the –NH– and –O– groups are stereochemically equivalent, with the oxygen atom having an electron pair lying in the same plane as its two bonds. Thus for rotation about Si–O or Si–N bonds, there are three energy minima with respect to the further bond to silicon, and three with respect to the N–H bond or oxygen lone pair. Thus the barrier to rotation about this bond is not high, being six-fold, and conformations are determined primarily by 1,3-interactions. This idea seems to work well for $NMe(SiH_2Me)_2$. In views along the N–Si bonds [Figure 5(*a*) and (*b*)] it can be seen that for one bond there is a *syn* Si–N–Si–H arrangement, while for the other there is an *anti* Si–N–Si–H arrangement. Viewed along the Si···Si axis [Figure 5(*c*)], the two SiH_2Me groups are seen to be mutually staggered, with an approximate *anti* C–Si···Si–C arrangement. The overall arrangement is extremely similar to that found in $O(SiH_2Me)_2$.[13] However, for $NMe(SiHMe_2)_2$, the position is more complicated. Compared with $NH(SiHMe_2)_2$, the Si–Me groups have twisted away from the N–Me group, so that there is one Si–N–Si–H arrangement nearly *syn*, but for the other Si–N bond there is a *syn* Si–N–Si–C grouping [Figure 6(*a*) and (*b*)]. Thus for the first time, when the Si···Si projection is considered [Figure 6(*c*)], we see two Si–Me groups nearly eclipsing each other. This is not a serious steric problem, as the carbon atoms involved are still 420 pm apart, but it is nevertheless a situation which seems to be avoided where possible.

Acknowledgements

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