The Structure of Bis(dimethylamino)silane in the Gas Phase, determined by Electron Diffraction

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We have studied the molecular structure of bis(dimethylamino)silane in the gas phase by electron diffraction. The molecule has no symmetry, the two dimethylamino groups having different CNC angles and conformations. Both nitrogens are non-planar, with the methyl groups displaced away from the other nitrogen in one case, towards it in the other case. The major structural parameters are r(SiN) 170.8 pm (both assumed equal), r(CN) 146.0 pm (all four assumed equal), and NSiN angle 112°. The asymmetry does not produce observable effects in the vibrational spectra, probably because the effects of coupling between dimethylamino groups are larger than any frequency differences due to the inequivalence. The vibrational spectra of the annealed solid are very similar to the i.r. spectrum of the gas, showing that no specific intermolecular association occurs on crystallisation.

As part of a systematic study[1,2] of the structures and conformations of silanes with Group 5B atoms attached to silicon, we have studied bis(dimethylamino)silane, to see whether the two dimethylamino groups adopt the same structure and conformation, or whether the two groups are different, as was found to be the case for the two formate groups in diformatosilane.[3] The bis-amine has been prepared before,[4] and its i.r.[4] and ^{1}H n.m.r. spectra[5] were reported. Here we report a study of the molecular structure in the gas phase by electron diffraction, together with a fuller study of the vibrational spectra.

Experimental

Bis(dimethylamino)silane was prepared by the reaction of dichlorosilane with dimethylamine in 1:4 molar ratio in the gas phase, using a two-bulb apparatus. A slight excess of dimethylamine over the exact 1:4 ratio gave the best results, the excess amine being removed by fractional condensation of the compound at 227 K. This is a modification[6] of the original preparation, which used di-iodosilane.[4] The compound was handled in a glass vacuum line with greased taps; it was identified by its molecular weight, 118 ± 3 by vapour density (theoretical, 118), and by its i.r. spectrum in the gas phase and its ^{1}H n.m.r. spectrum in solution [$\delta(^1H) = 2.43, 4.58$ p.p.m. in C_7D_8, lit.[5] 2.51 (CH), 4.38 (SiH) in cyclohexane, extrapolated to infinite dilution; ^1J(CH) = 133.2, ^1J(SiH) = 216.2, lit.[5] 133.4(5), 217.6(4) Hz].

Infrared spectra were recorded using a Perkin-Elmer 598 spectrometer, Raman spectra using a Cary 83 spectrometer with Ar$^+$ ion laser excitation at 488 nm, and ^{1}H n.m.r. spectra using a Bruker WP200 spectrometer. The electron diffraction patterns were recorded photographically on Kodak electron image plates using the Edinburgh apparatus,[7] and the plates scanned using a Joyce–Loebl MDM6 computer-controlled microdensitometer.[8] The electron wavelength and camera distances were derived from the analysis of scattering patterns for benzene, recorded consecutively with those of the compound. The electron wavelengths, the ranges of the scattering variable s for the two different camera distances used, the weighting points, correlation parameters, and scale factors found in the refinement[6] are listed in Table 1. The nozzle and sample were at room temperature during exposures. The scattering factors of Schäfer *et al.*[9] were used in the analysis, which used established data reduction[10] and refinement[8] programs.

Table 1. Camera distances, s ranges, and other parameters of the electron diffraction experiments

Camera distance (mm)	128.38	285.34
$s_{min.}$/nm^{-1}	60	20
s_{w1}/nm^{-1}	80	40
s_{w2}/nm^{-1}	300	124
$s_{max.}$/nm^{-1}	340	144
Δs/nm^{-1}	4	2
Correlation parameter	0.2343	0.2510
Scale factor	0.867(9)	0.736(18)
Electron wavelength (pm)	5.699	5.699

Results and Discussion

The gas-phase structure was derived from the molecular scattering intensities from the electron diffraction experiments, using a model which allowed the two dimethylamino groups to be inequivalent in respect of the SiN torsion angles, the dip angles defining the non-planarity of the nitrogen, and the CNC bond angles. No improvement was found to result from using inequivalent SiN or CN bond lengths, or from allowing the methyl torsion angles to differ in the two groups. The structure was therefore defined in terms of SiN, CN, CH, and SiH bond lengths, two CNC bond angles, the NSiN and HSiH bond angles, two dip angles (defined as the angle between the CNC plane and the SiN bond), two SiN torsion angles, a single methyl torsion angle, a single NCH bond angle, and a tilt angle for the SiH$_2$ group away from the plane bisecting the NSiN angle. The tilt angle did not prove to be refinable, but was fixed at a value giving the minimum R factor at a late stage of the refinement. The dip angles were defined so that zero corresponded to a planar nitrogen atom in each case, with positive dip angle implying a displacement of the methyl groups away from the other nitrogen. A zero SiN torsion angle corresponded to the plane bisecting the CNC angle coinciding with the NSiN plane, and positive displacement to a clockwise twist about the SiN bond in each case. The methyl torsion was defined as zero when one CH bond was *anti* with respect to the other CN bond, and it was assumed that all four methyl groups rotated in the same sense about the respective CN bonds. The possibility that the two SiNC angles in each dimethylamino group were unequal was investigated by introducing a 'wag' angle for each group, defined as zero when the two angles were equal, but no improvement was found, and both wags were finally fixed at zero.

The main bond distances and angles refined well, and the conformations of the two dimethylamino groups were well defined at the end of the refinement, with most of the amplitudes for distances not involving only hydrogen atoms refining at some stage to reasonable values. It did not prove possible to refine the amplitude for the C···C distance within each dimethylamino group, as it was strongly correlated with the two different CNC bond angles, so it was fixed at 6.0 pm, a value similar to those found in other dimethylaminosilanes.[1,2,11] The refinement converged well, giving good final *R* factors: $R_G = 0.063$, $R_D = 0.052$. The refined bond lengths (Table 2) are therefore well defined, with e.s.d.s of *ca.* 0.3 pm for the SiN, CN, and CH bond lengths. The SiH bond length could not be refined, as it contributes most directly to a peak at *ca.* 150 pm, which is mainly due to the CN bonded distances. It was therefore fixed at 148 pm, and the corresponding amplitude of vibration was fixed at the spectroscopic value, 8.8 pm. The HSiH bond angle was also kept fixed, and the tilt of the SiH_2 group out of the NSiN plane fixed at 3°. The positive sign corresponds to the SiH bonds being displaced towards the N atom (see below).

With up to 17 structural parameters it was necessary to refine many of the amplitudes of vibration in groups. This is shown in the list of distances (Table 3) by grouping such distances together. Table 3 contains a list of the main interatomic distances and amplitudes of vibration, and the most important correlations between refining parameters are shown in Table 4. The experimental molecular scattering intensity curve and the associated final differences are shown in Figure 1, and the radial distribution curve and final difference curve are shown in Figure 2.

The SiN bond length [170.8(3) pm] is significantly greater than in the (dimethylamino)monohalogenosilanes,[11] where SiN bond lengths of *ca.* 168 pm are found, and almost as long as those in dimethylaminosilane itself and the (dimethylamino)-methylsilanes $SiH_{3-n}Me_n(NMe_2)$, $n = 1, 2,$ or 3 (171.0—171.9 pm).[1,2] A comparison of various structural parameters is shown in Table 5. The mean CN bond length is reasonable, but the value found here for the amplitude of vibration (5.1 pm), which

Table 2. Molecular structure parameters:[a] distances (*r*) in pm, angles in °

SiN	170.80(30)
CN	146.00(20)
CH	111.67(40)
SiH	148 (fixed)
NSiN	112.1(35)
HSiH	108 (fixed)
NCH	109.9(8)
SiH_2 tilt	3 (fixed)[b]
[c] CNC, CN′C	108.4(10), 115.4(15)
[c,d] SiNC, SiN′C	122.6(13), 121.2(17)
[c] Dip, dip′	22.8(54), −14.4(87)
[c] SiN, SiN′ torsion	40.9(27), 17.5(30)
Methyl torsion	0 (fixed)[b]
Me_2N wag	0 (fixed)[b]

[a] Uncertainties (quoted in parentheses) are estimated standard deviations obtained in the least-squares refinement, increased to allow for systematic errors. [b] Fixed at a value giving minimum *R* factors. [c] The angles for the two distinct Me_2N– groups are given side by side to show how they differ. [d] The SiNC angles quoted are derived from the refining parameters, the CNC and dip angles.

Table 4. Correlation matrix (× 100) for refining parameters and amplitudes*

	Dip	NSiN	t(SiN)	*u*(Si···C)	Scale (short)
Dip	100	−83	−56	83	
Dip′	78	−94		85	
NSiN	−83	100	66	−91	
CNC′	−72		56	−62	
t(SiN)	−56	66	100	−62	
t(SiN′)	−76	88		−79	
u(CN)					65

* Only those correlation coefficients whose magnitude exceeds 55 are given. Where two parameters of a particular type are shown the first refers to the Me_2N– group with the dip angle of 22.8°, and all parameters for the other group are distinguished by a prime. t = Torsion angle. Scale (short) is the refined scale factor for the short camera distance.

Table 3. Interatomic distances and amplitudes (pm):* electron diffraction, r_a basis

	r	*u*		*r*	*u*
SiN	170.8(3)	5.6(2)	H(C)H	181.9(7)	11
CN	146.0(2)	5.1(2)	N(C)H	211.9(5)	10.5(4)
CH	111.7(3)	8.8(2)	N(Si)H	257.6(10)	15
SiH	148	8.8		262.6(9)	
C(N)C	236.8(9)	6	Si···H	277.9(12)	
C(N′)C	246.8(12)			284.9(8)	
C(N′)Si	276.2(16)	8.5		330.6(47)	18
C(N)Si	278.2(11)			337.0(65)	
N(Si)N	283.3(38)	10		359.2(25)	
C···N	345.7(25)			365.3(9)	
	349.3(35)	15.2(13)	C···H	261.8(16)	14.5
	378.1(16)			335.0(9)	
	413.6(34)				
C···C	397.3(22)				
	415.9(67)	14.8(16)			
	458.4(33)				
	520.2(14)				

* All distances contributing > 2% of the intensity of the largest peak in the radial distribution curve are included; the others are mainly long-distance C···H or H···H distances, whose contributions were included in the analysis, but are not listed here. Estimated standard deviations (e.s.d.s) are given (in parentheses) after values that were variable in the final stage of the refinement; those without an e.s.d. were fixed at the value given. For the non-bonded distances, X(Y)Z denotes the distance between atoms X and Z, both being bonded to a common atom Y; X···Z indicates two atoms not bonded to a single common atom.

Table 5. Structural parameters of some dimethylaminosilanes: electron diffraction r_a basis (distances in pm, angles in °)

	r(SiN)	r(CN)	d(C • • • C)	d(Si • • • C)	Dip	Ref.
$SiH_3(NMe_2)$	171.3(5)	145.7(6)	241.6(11)	276.1(6)	23.2(18)	1
$SiH_2Me(NMe_2)$	171.5(6)	145.3(3)	242.2(12)	276.9(1)	19.6(30)	1
$SiHMe_2(NMe_2)$	171.9(5)	146.0(4)	244.5(23)	274.6(12)	26.5(24)	1
$SiH_2(NMe_2)_2$	170.8(3)	146.0(2)	236.8(9) 246.8(12)	278.2(11) 276.2(16)	22.8(54) −14.4(87)	*
$SiH_2Cl(NMe_2)$	168.7(2)	146.4(2)	247.1(9)	274.2(3)	−17.2(11)	11
$SiMe_3(NMe_2)$	171.0(5)	146.2(4)	249.4(16)	277.0(7)	0 fixed	2

* This work.

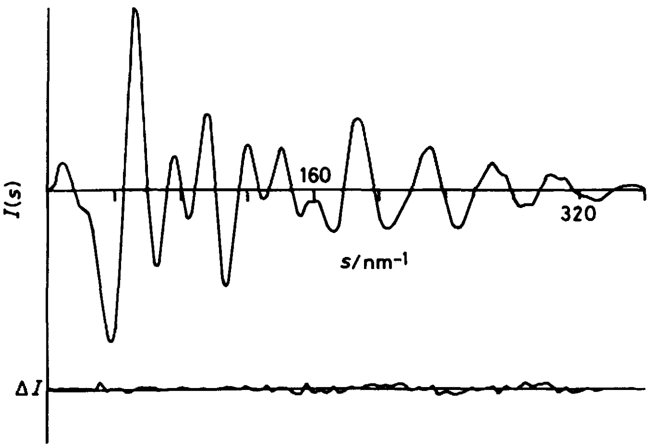

Figure 1. Combined molecular scattering intensity (observed and final weighted difference curves) for bis(dimethylamino)silane

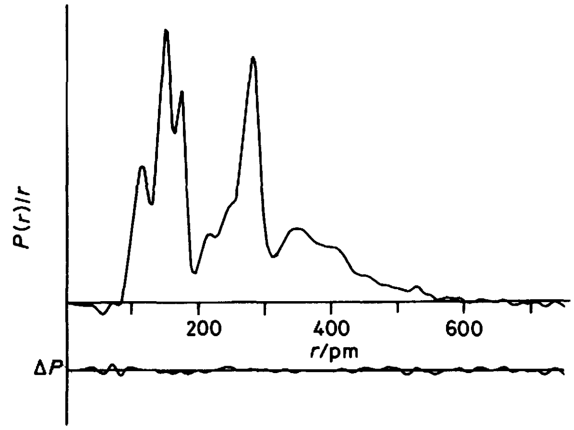

Figure 2. Observed and final difference radial distribution curves for bis(dimethylamino)silane. Before Fourier inversion the data were multiplied by $s \cdot \exp[-0.000\,02\, s^2/(Z_{Si} - f_{Si})(Z_N - f_N)]$

is *ca.* 0.9 pm larger than expected,[1,2,11] suggests that there may be slight differences in length between the four distinct CN bonds in the structure. The most striking result is that the two dimethylamino groups are indeed inequivalent, with CNC bond angles differing by some 7°. This corresponds to a difference in the C • • • C distances within the groups of over 10 pm; the distance is smaller in the group containing atom N, larger in the group containing atom N′. We cannot, however, be sure that this difference is genuine, because we have been unable to refine the C • • • C amplitude of vibration, which must be strongly correlated with the differences in distances and angles. The C • • • C peaks in the radial distribution curve (Figure 2) are on the short side of the much stronger peak due to the Si • • • C distances, and this again must contribute to some uncertainty in the CNC bond angles. The conformations about the SiN bonds are also different, torsion angles of about 41 and 17.5° being found for the atoms N and N′, with e.s.d.s of only 2° in each case. Most strikingly, the two dimethylamino groups have dips of opposite signs, so that the methyl groups on atom N are displaced away from the other nitrogen (N′), whereas those on atom N′ are displaced towards the other nitrogen (N). The difference in dip angles is thus highly significant, despite the large e.s.d.s. The dip angles correspond to sums of valence angles at the two nitrogens of 357 (N) and 353° (N′). As mentioned above, no significant difference could be established in the SiN bond distances in the two groups, and the best R factors were obtained when the CN torsion angles were held at zero, so that one CH bond in each methyl is *anti* with respect to the other CN bond. The NSiN′ angle was rather large (112°) but had a large uncertainty, and it was quite strongly correlated with the dip angles. We cannot therefore be sure that the apparent deviation from the tetrahedral angle is significant.

The most securely established differences between the two dimethylamino groups are in the dips and the SiN torsion angles. These are such that one methyl group lies between the two SiH bonds, while the other three are approximately *anti* with respect to SiH about their respective SiN bonds (see Figure 3, which shows the molecule from various directions). The fact that the two groups have dips of opposite sign can be understood in terms of steric repulsions between methyl groups and the effects of the two nitrogen lone pairs; if both dips were positive, so that all methyl groups were displaced away from the other nitrogen, the two lone pairs would be pointing towards each other, whereas if both were negative the two lone pairs would be well away from each other, but the methyl groups would be forced into close contact. In the conformation actually found, the shortest inter-group contacts (taking each Me_2N– and the SiH_2 fragment as a group) are SiH • • • CH distances of *ca.* 249 pm, and the shortest CH • • • CH contact is 279 pm. The first of these is about the sum of the van der Waals radii, the second rather longer, but it does seem reasonable to invoke steric repulsions between groups to account for the observed conformations. The two dimethylamino groups are twisted about 60° with respect to each other, thus minimising contacts between methyl groups. The shortest CH • • • CH contacts within dimethylamino groups are 237 pm in one group, 255 pm in the other.

The molecule has no symmetry elements other than the identity, and it is possible in principle that the two different Me_2N– groups have distinct vibration frequencies. This sort of behaviour was found[3] for the two different formate groups in diformatosilane, where the two groups are quite different in their conformations, and two distinct C–O bond stretches can be seen in the i.r. spectrum. In the present case, however, we may

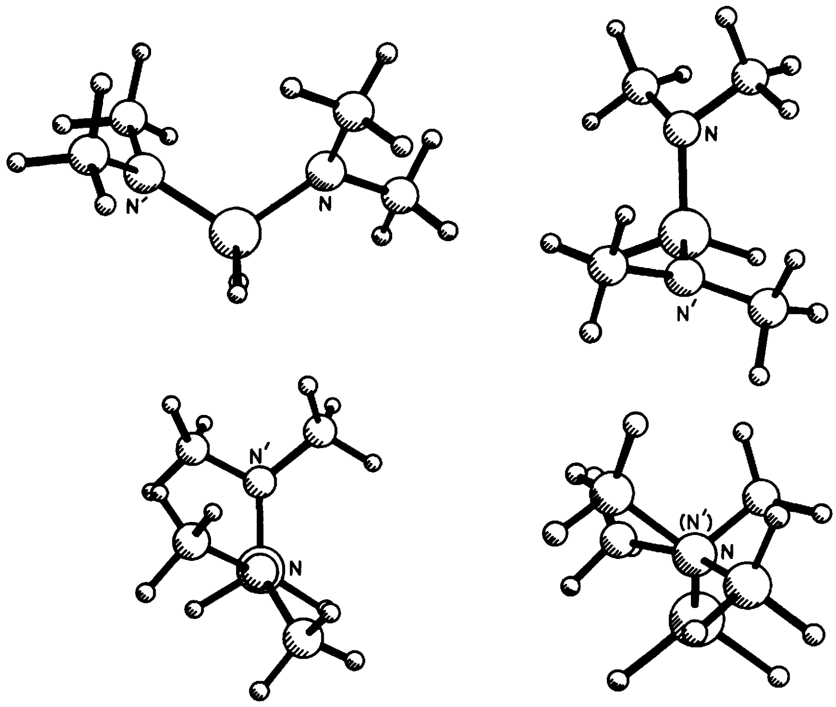

Figure 3. The molecular structure of bis(dimethylamino)silane, viewed from various directions

expect that the CN stretches will give two coupled modes for each group (symmetric and asymmetric combinations of the two CN bond motions), and that the symmetric combinations will couple with the SiN bond stretch as in other dimethylaminosilanes.[6] The two SiN stretches will then couple to give symmetric and antisymmetric modes in turn, and the small frequency differences due to the two distinct Me_2N– group conformations will be lost in the larger shifts due to the strong couplings between modes. Only for the asymmetric CNC group stretches might we expect to see two bands at slightly different frequencies; this mode is assigned to bands at *ca.* 1 185 cm^{-1} in the (dimethylamino)halogenosilanes,[6] and we assign the strong i.r. band at 1 189 cm^{-1} in the gas-phase spectrum (Table 6) to the corresponding mode in the bis-amine. There is a weaker band at lower frequency, *ca.* 1 155 cm^{-1} in the gas phase, which becomes more distinct, but still weak, in the spectrum of the solid.

In the Raman spectrum of the solid the lower frequency band is weak, but the higher frequency band is even weaker, and it is more likely that the two bands are due to the two (in-phase and out-of-phase) combinations of the two asymmetric CNC stretches than to the distinct modes due to the distinct Me_2N– groups. A weak peak to higher frequency of the band assigned to the symmetric CNC stretches near 1 300 cm^{-1} in the spectrum of the solid is likely to be due to an overtone or combination, as it is weaker than the main band in both the i.r. and the Raman spectrum. In all there are six heavy-atom bond stretches, the various combinations of which are assigned to four or five bands between 650 and 1 305 cm^{-1}; this region also includes methyl rocks (eight modes expected) and at least three out of the four SiH_2 group deformations. Only one distinct band can be assigned to a methyl rock; the others are presumably hidden under stronger bands arising from other modes. There are two bands between 300 and 400 cm^{-1} in the i.r. and Raman spectra of the solid, where we might expect to find CNC angle bending modes, and it is possible that these might be due to the two different Me_2N– groups, but again the two bands could equally well be explained as arising from coupling between the bends of the two groups. One other effect of the inequivalence of the two Me_2N– groups might be to make the SiH_2 twisting motion active in the i.r.: it would be an a_2 mode, and hence i.r.-inactive if the molecule had two equivalent Me_2N– groups and C_{2v} symmetry overall. This mode is assigned to the Raman band at 772 cm^{-1} in the solid, and also appears in the i.r. spectrum of the solid, but is

Table 6. Vibrational spectroscopic data (cm^{-1}) for bis(dimethylamino)silane*

Phase Technique	gas i.r.	solid i.r.	solid Raman
ν(CH)	2 960s	2 970s	2 980m
		2 955s	2 900m
	2 867s	2 860s	2 880m
		2 840s	2 850m
	2 800s	2 795s	2 800m
ν(SiH)	2 132s	2 112s	2 120vs
δ(CH_3)	1 480m	1 477m	1 490m
	1 450m	1 442m	1 440ms
	1 410vw	1 410w	1 412mw
		1 339w	
$\nu_{sym.}$(CNC)	1 297s	1 305s	1 305m
$\nu_{asym.}$(CNC)	1 189s	1 192s	1 190vw
		1 153w	1 153mw
ρ(CH_3)	1 071w	1 080m	1 080w
$\nu_{asym.}$(NSiN)	997s	1 005s	1 007m
SiH scissors	955m	952m	953m
SiH wag	920vs	920vs	
SiH twist		770w	772m
SiH rock	698w	698s	710m
$\nu_{sym.}$(NSiN)	657m	652vs	650vs
δ(CNC)		387m	395m
		321w	331w
δ(NSiN) δ(CNSi)		260m	232w
			150w

* s = Strong, m = medium, w = weak, v = very. The i.r. spectra were not studied below 400 cm^{-1} in the gas or below 200 cm^{-1} in the solid phase.

much weaker in the i.r. spectrum of the gas, and we cannot be sure whether its appearance in the solid is due to an essential asymmetry of the molecule or to distortions induced by intermolecular forces. There is thus no clear-cut evidence from the i.r. and Raman spectra that the two Me_2N– groups are inequivalent; such evidence would in any case depend on the coupling between the groups being small compared with the frequency differences due to the inequivalence for the various modes.

One clear conclusion can be drawn from the similarity between the i.r. spectra in the gas and solid phases; there is no sign of any dramatic change in the molecular structure on crystallisation, such as is found for dimethylaminosilane[12] and the (dimethylamino)monohalogenosilanes.[6] Equally, the similarity between the i.r. and Raman spectra of the solid phase argues that there are no strong centrosymmetric molecular associations in the solid (which was carefully annealed in each case). Thus, unlike dimethylaminosilane[12] and its monohalide derivatives,[11] bis(dimethylamino)silane appears not to form dimers, oligomers, or strongly-associated chains in the crystal.

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