Molecular Structures of Some (Dimethylamino)halogenosilanes in the Gas Phase by Electron Diffraction and the Crystal and Molecular Structures of Mono- and Di-chloro(dimethylamino)silane by *X*-Ray Diffraction at Low Temperatures †

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The (dimethylamino)halogenosilanes $SiH_2X(NMe_2)$ (X = Cl, Br, or I) have monomeric structures in the gas phase, with the three bonds at nitrogen close to coplanarity, but not exactly so; $SiHCl_2(NMe_2)$ is also monomeric, with the nitrogen apparently planar. The conformations about the Si–N bonds suggest that repulsions between the nitrogen lone pair and the halogen atom(s) on Si are important. Dichloro(dimethylamino)silane retains its monomeric structure in the crystal at 94 K, and the molecular parameters are close to those found for the gas phase; molecules are associated only very loosely through bridging Cl atoms. In strong contrast, the crystal structure of monochloro(dimethylamino)silane at 116 K shows it to consist of dimers in the solid state, in which two strongly-distorted monomer units are linked through their nitrogen and silicon atoms in a four-membered ring. The two bonds to nitrogen formed by each silicon are not equivalent [bond lengths 181.3(13) and 205.4(13) pm; *cf.* 168.7(2) pm in the gas-phase monomer], but the silicon atoms are clearly five-co-ordinate, with the five bonded groups defining a trigonal bipyramid; Cl and one of the two nitrogen atoms occupy apical positions. The nitrogen atoms are four-co-ordinate, with roughly tetrahedral bond angles. The structure is compared with that of dimethylaminosilane itself, which forms a cyclic pentamer in the crystal.

As part of a continuing study of the structures and conformations of silicon derivatives of elements of Main Groups 5 and 6 of the Periodic Table[1,2] we have prepared[3] and characterised some (dimethylamino)halogenosilanes, and report here the determination of their structures in the gas phase by electron diffraction. As reported earlier,[3,4] the vibrational spectra of chloro(dimethylamino)silane show a distinct change on crystallisation, and we have investigated the crystal structure of this compound and of dichloro(dimethylamino)silane by *X*-ray diffraction. The crystal structure of the monochloride has been reported earlier;[4] we report here the crystal structure of the dichloride and discuss the structural results for the whole series of compounds.

Experimental

The compounds were prepared, purified, and characterised as reported earlier;[3] they were handled under vacuum to avoid hydrolysis and oxidation.

Electron Diffraction.—Electron diffraction patterns were obtained photographically on Kodak Electron Image plates using the Edinburgh apparatus,[5] and plates were scanned by the S.E.R.C.-funded service at Daresbury using a computer-controlled Joyce–Loebl MDM6 microdensitometer,[6] giving scattering data in the range 20—344 nm^{-1} of the scattering variable, *s*. The data were analyzed using established data reduction[6] and model refinement[7] programs. The *s* ranges and intervals, weighting points, correlation parameters, and scale factors for the two different camera distances used for each compound, and the electron wavelengths (determined by analysis of the diffraction patterns of gaseous benzene recorded consecutively with those of the compounds) are listed in Table 1. The nozzle was at room temperature for all the compounds reported here; the samples were also held at room temperature except in the case of the most volatile, chloro(dimethylamino)-silane, which was held at 273 K during the exposure of the plates. Some problems were encountered with the photographic plates, especially with bromo(dimethylamino)silane, which appears to react chemically with the emulsion, leaving a moisture-sensitive surface layer that resulted in patchy development; this was avoided as much as possible by exhaustive pumping after exposure before allowing air to enter the apparatus and removing the plates. Two long-distance sets of plates were obtained for the iodo-compound, and both were used in the analysis. The scattering factors of Schafer *et al.*[8] were used in all calculations.

Crystallography.—For the *X*-ray diffraction studies, samples of the compounds were sealed in Pyrex glass capillaries. Crystal growth was monitored using a Weissenberg camera as described earlier, and the crystals transferred to a diffractometer without melting.[9] The samples were examined at 94 K for the dichloride and 116 K for the monochloride, the temperature being maintained within about ±3 K by a controlled stream of cooled nitrogen. The crystal data for monochloro(dimethylamino)-silane have already been reported;[4] the data for the dichloro-silane are given below. Analysis used the established programs SHELX 76[10] and SHELX 84,[11] implemented on ICL 2900 series computers in Edinburgh.

Crystal data for dichloro(dimethylamino)silane. $C_2H_7Cl_2NSi$, M = 144.04, monoclinic, a = 631.29(10), b = 1 107.9(7), c = 984.5(3) pm, β = 104.360(22)°, U = 0.6671 nm^3 (from 24 centred reflections with θ = 7.6—12.3° at 94 K), Z = 4, D_c = 1.434 g cm^{-3}, $F(000)$ = 296, λ(Mo-K_α) = 0.710 73 Å, μ(Mo-K_α) = 9.49 cm^{-1}, space group $P2_1/c$ from systematic absences; colourless cylindrical crystal, 0.4 × 0.4 × 0.5 mm.

Data collection and processing. CAD4 diffractometer with

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

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

Compound	$SiH_2Cl(NMe_2)$		$SiH_2Br(NMe_2)$		$SiH_2I(NMe_2)$			$SiHCl_2(NMe_2)$	
Camera	Short	Long	Short	Long	Short	Long	Long	Short	Long
distance/mm	128.37	285.45	128.36	285.30	128.26	285.32	286.01	128.40	285.19
$s_{min.}/nm^{-1}$	60	20	60	20	80	20	20	68	20
sw_1/nm^{-1}	80	40	80	40	100	40	40	80	40
sw_2/nm^{-1}	300	120	300	120	240	124	124	300	120
$s_{max.}/nm^{-1}$	340	146	344	144	280	140	140	340	144
$\Delta s/nm^{-1}$	4	2	4	2	4	2	2	4	2
Correlation	−0.174	0.245	−0.166	0.469	−0.343	0.401	0.448	0.108	0.477
Scale factor	0.701	0.636	0.727	0.810	1.016	0.961	0.949	0.735	0.791
Uncertainty	13	8	26	10	59	19	21	17	23
Electron wavelength/pm	5.709	5.708	5.704	5.708	5.677	5.677	5.676	5.705	5.705

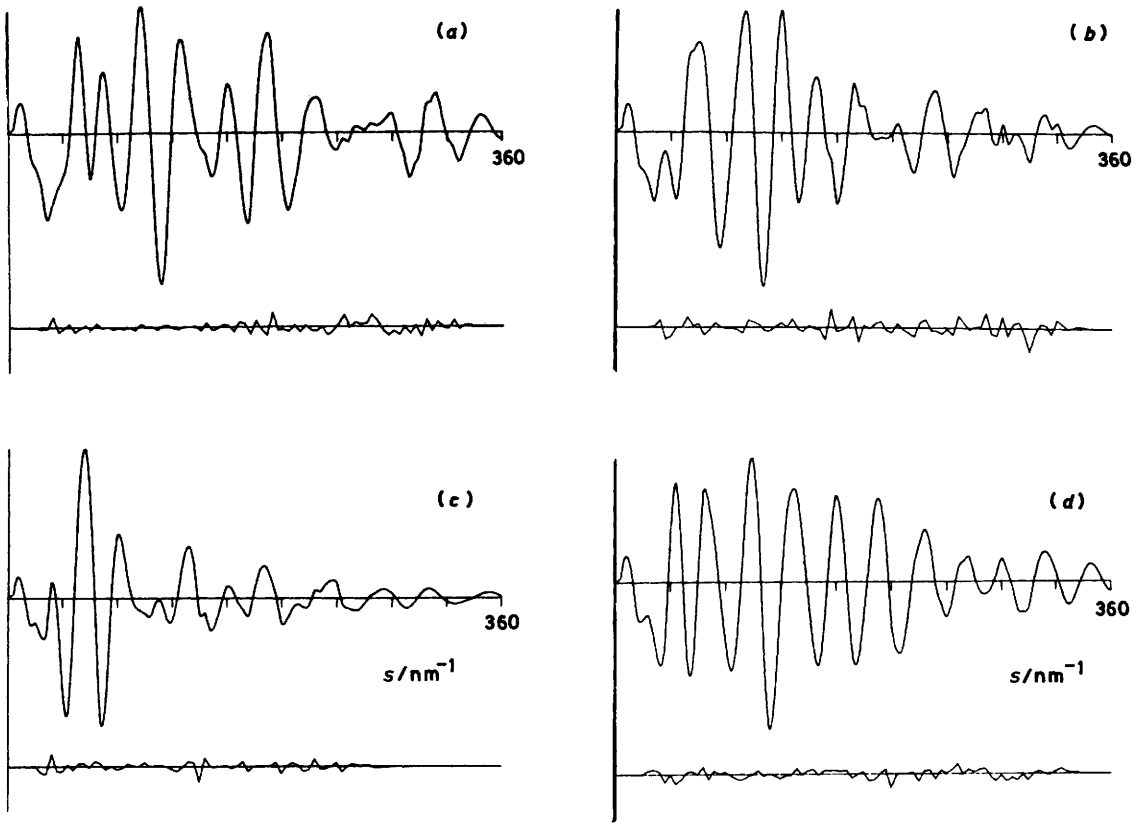

Figure 1. Combined electron scattering intensities (observed and final difference curves) for (*a*) $SiH_2Cl(NMe_2)$, (*b*) $SiH_2Br(NMe_2)$, (*c*) $SiH_2I(NMe_2)$, and (*d*) $SiHCl_2(NMe_2)$

low-temperature attachment, $\omega-2\theta$ scans, 2 134 data measured ($\theta_{max.}$ = 30°; h −8—8, k 0—15, l 0—13), 1 920 unique, giving 1 696 with $F > 2\sigma(F)$ for structure solution and refinement. Crystal showed no significant movement or decay over 54 *X*-ray hours.

Structure solution and refinement. Automatic direct methods[11] located all non-H atoms and subsequent iterative least-squares cycles and difference Fourier syntheses revealed the positions of the hydrogen atoms. For refinement[10] H atoms were treated as isotropic and all other atoms as anisotropic: at convergence R, R' were 0.0453, 0.0655, S = 1.23 for 83 parameters. Maximum and minimum residuals in the final ΔF synthesis were 0.75 and −0.88 e Å^{-3} respectively, and the weighting scheme $w^{-1} = \sigma^2(F) + 0.001\,092\,F^2$ gave satisfactory agreement analyses. Fractional atomic co-ordinates are given in Table 2.

Results

Gas-phase Structures.—These were established by analysis of the electron diffraction patterns, using models assuming only monomeric species to be present. Methyl groups were assumed to have local three-fold symmetry, and it was also assumed that the two methyl groups for each compound were equivalent. The non-planarity of the nitrogen atom was defined explicitly as a dip angle between the Si–N bond and the plane defined by the three heavy atoms of the dimethylamino group. The conformation was defined in terms of a torsion angle about the Si–N bond; for the monohalides this angle was defined as zero when the halogen atom was in the CNC angle bisector plane. For a torsion angle near zero, a negative dip angle (as was found for the monohalogeno-compounds) corresponds to the methyl groups being displaced *towards* the halogen. The methyl torsion angles were also varied together, either by least-squares refine-

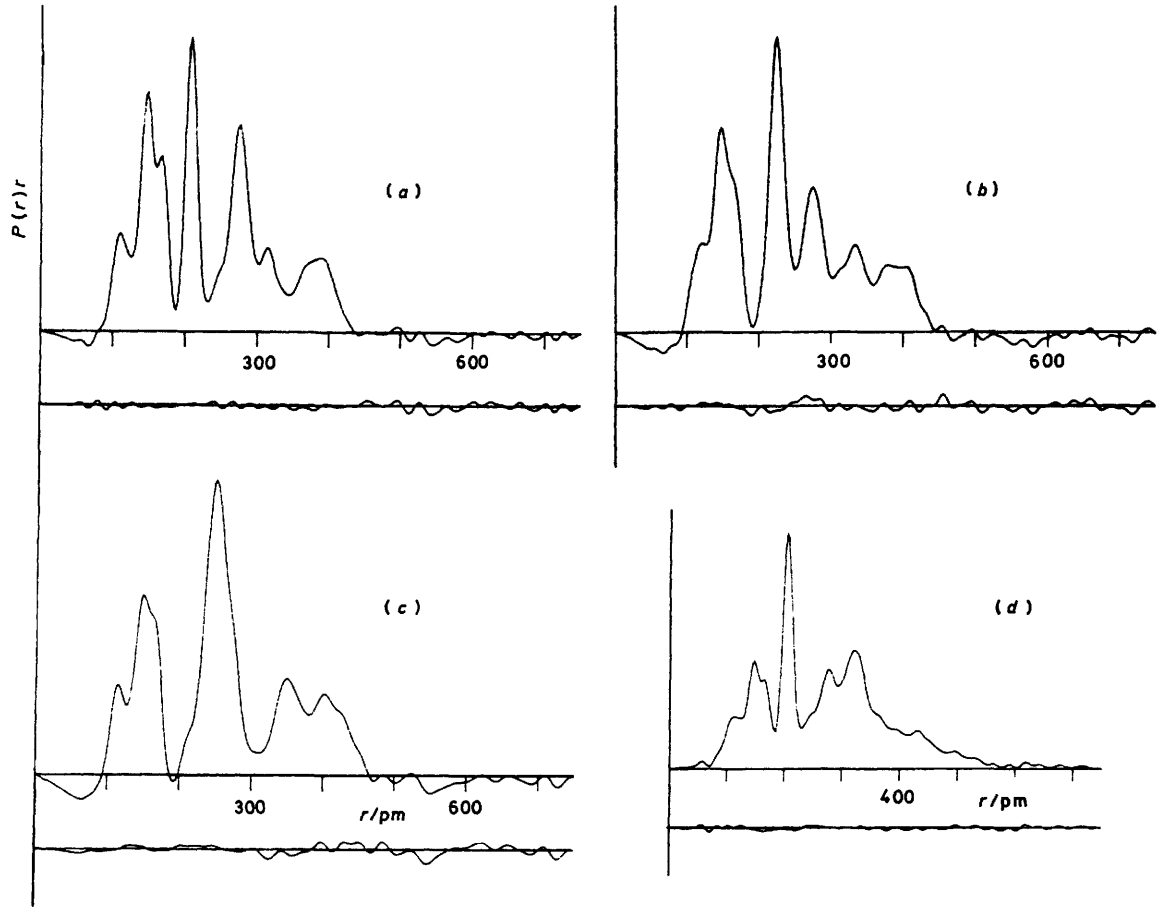

Figure 2. Observed and final difference radial distribution curves for (*a*) $SiH_2Cl(NMe_2)$; (*b*) $SiH_2Br(NMe_2)$; (*c*) $SiH_2I(NMe_2)$, and (*d*) $SiHCl_2(NMe_2)$. Before Fourier inversion the data in each case were multiplied by $s \exp[-0.000\,02s^2/(Z_{Si} - f_{Si})(Z_X - f_X)]$, where X is the halogen atom concerned

Table 2. Fractional atomic co-ordinates with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cl(1)	0.522 51(9)	0.862 57(6)	0.340 55(6)
Cl(2)	0.042 79(10)	0.964 50(5)	0.193 04(6)
Si(1)	0.199 90(9)	0.811 06(5)	0.282 95(6)
N(1)	0.110 6(3)	0.764 39(15)	0.419 54(19)
C(1)	0.011 0(4)	0.646 78(18)	0.427 28(25)
C(2)	0.123 2(4)	0.839 13(20)	0.543 03(25)
H(1)	0.175(5)	0.720(3)	0.186(3)
H(11)	−0.143(5)	0.651 7(25)	0.429(3)
H(12)	0.097(7)	0.590(4)	0.517(4)
H(13)	0.006(6)	0.598(4)	0.346(4)
H(21)	0.203(5)	0.800(3)	0.629(3)
H(22)	0.210(5)	0.919(3)	0.541(3)
H(23)	−0.034(5)	0.856 7(25)	0.554(3)

ment or by investigation of the variation of the overall fit (expressed as an *R* factor) as they were altered step-wise. This is indicated by the Tables by the expression 'fixed' after the value. A zero methyl torsion angle corresponded to one C–H bond *trans* to the other N–C bond; methyl groups were assumed to rotate in the same sense. There were no particular difficulties in the refinement; the main structural parameters were well defined from the beginning in each case, and the refinements converged fairly smoothly. The structural parameters found for the three (dimethylamino)monohalogenosilanes are given in Table 3, together with the *R* factors, R_G and R_D, for each refined structure; the molecular intensity curves and final differences are

Table 3. Structural parameters for $SiH_2X(NMe_2)$ (X = Cl, Br, or I) in the gas phase by electron diffraction (r_a basis); distances in pm, angles in °

Compound	$SiH_2Cl(NMe_2)$	$SiH_2Br(NMe_2)$	$SiH_2I(NMe_2)$
r(SiN)	168.7(2)	168.4(4)	167.0(2)
r(SiX)	207.0(1)	224.9(2)	244.6(3)
r(SiH)	147.0(17)	150 (fixed)	150 (fixed)
r(NC)	146.4(2)	147.2(3)	146.8(3)
r(CH)	110.2(4)	115.5(8)	113.1(3)
CNC	115.1(6)	109.8(14)	117.3(12)
HSiH	111 (fixed)	108 (fixed)	108 (fixed)
NSiX	113.2(3)	114.7(6)	115.1(4)
NCH	111.6(8)	106.4(21)	108.6(5)
HSiX	105.6	105.3	107.3
HSiN	110.6	111.5	109.4
SiNC	120.8(3)	121.3(5)	119.1(4)
Dip*	−17.2(11)	−25.4(16)	−20.8(11)
SiN (torsion)	9.7(51)	−14.1(12)	0 (fixed)
CN (torsion)	0 (fixed)	15.6(47)	0 (fixed)
R_G	0.084	0.149	0.120
R_D	0.081	0.126	0.086

* Dip angle (see text).

Table 4. Interatomic distances (d/pm) and amplitudes of vibration (u/pm) for gaseous $SiH_2X(NMe_2)$ (X = Cl, Br, or I)*

Compound	$SiH_2Cl(NMe_2)$		$SiH_2Br(NMe_2)$		$SiH_2I(NMe_2)$	
	d	*u*	*d*	*u*	*d*	*u*
CN	146.4(2)	4.0(2)	147.2(3)	4.7(4)	146.8(3)	6.0(4)
SiN	168.7(2)	4.8(2)	168.4(4)	6.0(4)	167.0(2)	4.8(4)
SiX	207.0(1)	4.7(1)	224.9(2)	6.2(3)	244.6(3)	7.5(4)
C···C	247.1(9)	7.4	240.9(22)	13.4(52)	250.8(18)	7.5(4)
C···Si	274.2(3)	7.1(3)	275.3(6)	8.5(6)	270.7(5)	8.7(5)
N···X	314.4(5)	8.5(6)	332.6(10)	11.2(9)	349.8(7)	10.9(8)
C···X	375.8(47) 396.3(60)	17.1(63)	382.1(16) 412.4(16)	14.2(24)	413.0(12)	35.2(34)
C–H	110.2(4)	8.1(4)	115.5(8)	8.5(7)	113.1(3)	5.2(5)
Si–H	147.0(17)	8.8(4)	150	8.8	150	8.8
N···CH	213.2(10)	10.3	210.6(25)	11	211.9(6)	5.1(8)
N···SiH	259.8(14)	12	263.4(5)	12	259.0(3)	12
C···CH	276.5(20) 342.5(11)	17	249.8(50) 276.3(68) 337.4(24)	17	227.7(23) 345.0(13)	17
C···SiH	303.0(26) 314.9(37) 390.8(23) 395.3(15)	20	308.7(12) 328.2(13) 395.5(8) 400.4(5)	20	305.1(12) 392.4(5)	20
X···SiH	284.3(12)	11.6(5)	301.2(4)	9.1	322.7(4)	18.3
X···CH	368.5(95) 379.2(42) 400.5(79) 403.7(90) 483.4(43) 500.3(47)	25	348.8(79) 379.2(65) 387.7(82) 443.7(70) 492.9(25) 511.6(35)	20	400.2(27) 410.5(12) 522.2(12)	14.7(21)
Si···CH	279.9(12) 333.7(13) 359.2(9)	9.2(24)	270.0(37) 285.1(43) 309.1(52) 335.1(50) 355.6(33) 367.2(20)	11	271.9(15) 325.3(11) 357.5(9)	18

* Estimated uncertainties are given in brackets after each distance or amplitude; where no uncertainty is given the quantity involved was fixed at the value given in the final refinement. Distances involving only H atoms are not listed, but were included in the calculations of molecular intensity; they contribute only very little to the total calculated intensity.

shown in Figure 1, and the radial distribution curves with final differences in Figure 2. Lists of the non-bonded interatomic distances are given in Table 4, with refined or assumed amplitudes of vibration; distances involving only hydrogen atoms are not listed, but were included in the calculations of molecular scattering intensity. The correlation matrices showing the largest correlation coefficients between refining parameters are given in Table 5.

The structures all appear to have nitrogen atoms that are not quite planar; the dip angles, which would be zero for planar nitrogen atoms, are *ca.* −20°, with estimated standard deviations (e.s.d.s) of only a few degrees. The sum of valence angles around nitrogen, which would be 360° for a strictly planar atom, has values ranging between 351 and 357°, with e.s.d.s. of 1 or 2°. As a result of the non-planarity, which we believe to be genuine, and not simply an expression of shrinkage, the molecules have at most a single mirror plane of symmetry, which can only be a true symmetry element for the molecule if the single halogen atom lies on the plane bisecting the CNC angle. This is apparently so for the iodide, where the best fit was obtained with the SiN torsion angle set at zero, so that the iodine atom is in the bisecting plane, as far from the methyl groups as is possible. For the chloride and the bromide the SiN torsion angles refined to non-zero values (Table 3), but these are close to zero (the signs are not significant); we are not sure whether they are an expression of shrinkage relating to a low-frequency torsional motion about the Si–N bond, or represent genuine departures from the C_s structure. In each case, then, the planes defined by the CNC and NSiX groups (X is halogen) are essentially perpendicular.

The bond lengths are well defined for the heavy atoms; C–H bond lengths refined to reasonable values, but Si–H bond lengths had to be fixed at values giving a minimum R factor, as the Si–H distance is close to the C–N distance, which has a much greater contribution to the scattering. The C–N bond lengths are very similar for the three compounds, and the variations in the Si–N distances are small, but probably significant; all are definitely smaller than the Si–N distance in the parent dimethylaminosilane, 171.5(4) pm. The CNC angle found for the bromide is apparently anomalous; the data are poor for this compound, probably because of the reaction noted with the emulsion (as shown by the high R factors), and we do not believe that the discrepancy is significant. All the SiNC angles are close to 120°, and the Si···C distances (Table 4) close to 275 pm.

The dichlorosilane structure is somewhat different from those of the monohalides; here the nitrogen appears to be much closer to planarity, the dip angle that gave the minimum R factor being only 6°, and the sum of valence angles 359°. The e.s.d. for the sum of *ca.* 1° is not a true measure of the uncertainty because the dip angle was fixed. An attempt to refine the dip angle together with the CNC angle gave a value of 6° with an e.s.d. of 8°; the e.s.d. of the CNC angle rose from 0.6 to 1.0°, showing that the correlation in these two parameters is not excessive. The

Table 5. Correlation matrices (×100) for refining parameters and amplitudes for $SiH_2X(NMe_2)$ (X = Cl, Br, or I)*

(*a*) X = Cl

	r(SiH)	NCH	*u*(CN)	*u*(SiCl)	*u*(C···Cl)	*u*(Si···H)
r(NC)	−83					
r(SiCl)		−59				
CNC		60				
SiN (torsion)					−98	
u(C···Si)						−65
u(N···Cl)						56
Scale (s)			54	74		

(*b*) X = Br

	CNC	BrSiN	*u*(C···C)	Scale (s)
r(SiBr)			77	
Dip	64	−58		
NCH				−55
u(CN)				52

(*c*) X = I

	CNC	ISiN	*u*(SiN)	*u*(Si···C)	*u*(I···C)	Scale (s)
r(SiI)	−81					
Dip	69					
u(CH)						68
u(CN)			76			67
u(SiN)			100			70
u(SiI)			52	74		
u(I···N)					54	
u(I···H)		−58			−74	

* Entries whose absolute magnitude is less than 50 are omitted. Scale (s) is the scale found for the short camera distance.

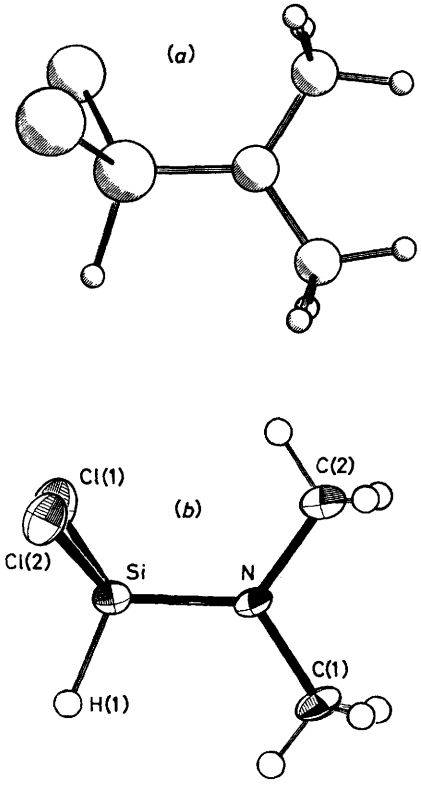

Figure 3. Molecular structures of $SiHCl_2(NMe_2)$; (*a*) in the gas phase by electron diffraction, and (*b*) in the crystal at 94 K by *X*-ray diffraction

Table 6. Structural parameters, interatomic distances, and amplitudes for $SiHCl_2(NMe_2)$;* bond lengths in pm, angles in °

(*a*) Structural parameters

	Gas (e.d.)	Crystal (*X*-ray)
r(SiN)	168.1(4)	166.4(2)
r(SiCl)	205.6(1)	205.5(1)
r(SiH)	150 (fixed)	137(3)
r(NC)	146.4(3)	145.7(3)
r(CH)	112(1)	96—110
CNC	115.5(6)	113.6(2)
ClSiCl	104.8(7)	103.2(3)
ClSiN	111.0	112.0, 112.4(1)
HSiN	108 (fixed)	109(1)
SiN (torsion)	76(1)	87(1)
CN (torsion)	60 (fixed)	2(3), −7(2)
Dip (see text)	6 (fixed)	0
Sum of angles at N	359.6(12)	360.0(3)

(*b*) Interatomic distances and amplitudes of vibration (pm) in the gas phase

	d	*u*		*d*	*u*
CN	146.4(3)	4.4(3)	Cl···SiH	294.8(3)	18.4
SiN	168.1(4)	5.5(4)	Cl···CH	319.0(37)	
SiCl	205.6(1)	5.1(1)		331.0(41)	
C···C	247.6(10)	7.7		374.4(32)	
C···Si	275.3(4)	7.8(5)		394.2(52)	
Cl···N	308.7(4)	18.5(27)		427.5(24)	
Cl···Cl	325.7(16)	12.1(8)		453.7(43)	20
Cl···C	350.2(14)	17.3(39)		457.6(15)	
	369.4(13)	15.2(27)		462.0(15)	
	407.8(16)	15.1(32)		478.1(30)	
	436.4(10)	11.2(19)		489.4(26)	
CH	112.1(8)	9.8		494.2(30)	
SiH	150	8.8		518.3(27)	
N···CH	217.8(26)	15.3	Si···CH	304.0(34)	
N···SiH	257.5(3)	12		314.1(32)	18
C···CH	257.0(41)	17		372.7(20)	
	326.5(23)		C···SiH	295.5(6)	20
				394.9(4)	

* Estimated standard deviations of refining parameters, interatomic distances, and amplitudes are given in parentheses; where no e.s.d. is shown the value was fixed in the final refinement. Distances involving only H atoms are not listed, but were included in the calculations of molecular scattering intensity.

correlation coefficient is calculated to be −0.8, and the range of values possible for the sum of angles at N is 358—360°. The torsion angle about the Si–N bond is close to 90°, which would correspond to the CNC plane bisecting the Cl–Si–Cl angle if the nitrogen were planar, so one methyl group lies between the two Cl atoms, the other more or less eclipsing the Si–H bond [Figure 3(*a*)]. The torsion angle is strongly correlated with the dip angle, (correlation coefficient 0.96), so the uncertainty rises sharply to about +8° if the dip angle is allowed to refine, but the value found does not alter significantly. The Si–N bond length is very similar to that found for the monochloride, and the dimethylamino-group parameters are also very much the same for the two chlorides. The major difference in bond angles is that the SiNC angles are larger for the dichloride, which account for the large sum of bond angles at N, and hence its planarity. The CN torsion angle was fixed at 60° to give the best final *R* factor.

The final parameters are given in Table 6, with the important interatomic distances and the associated amplitudes; the molecular intensity curve and final differences, and radial distribution curve with final differences are shown in Figures 1(*d*) and 2(*d*) respectively. The final *R* factors were R_G 0.098,

Table 7. Correlation matrix (× 100) for refining parameters and amplitudes for $SiHCl_2(NMe_2)$*

	u(Cl ··· Cl)	u(N ··· Cl)	u(C ··· Cl)	u(C ··· Cl)	Scale (s)	Scale (l)
NCH	63				52	62
ClSiCl		−86				
SiN (torsion)			53	58		
u(SiCl)					81	
u(C ··· Si)		59				
u(C ··· Cl)			100	76		
u(C ··· Cl)	72					
u(C ··· Cl)				68		
Scale (l)	59					100

* Entries whose absolute magnitude is less than 50 are omitted. Scale (l) is the scale found for the long camera distance.

Table 8. Structural parameters of the dimer of chloro(dimethylamino)-silane in the crystal at 116 K; distances in pm, angles in °

r(SiN)	181.3(13)	CNC	108.4(10)
r(SiN')	205.4(13)	HSiH	117(2)
r(SiCl)	223.1(6)	NSiCl	96.1(5)
r(SiH)	149(11)	NCH	105.5—114.4
r(NC)	150.3(18)	HSiCl	80.9(40)
r(CH)	108(2)	HSiN	125.7(41)
		SiNC	112.7(9)
		NSiN'	83.0(5)
		SiNSi'	97.0(6)

R_D 0.084. The correlation matrix for the final refinement (showing only the largest terms) is given in Table 7.

Solid-phase Structures.—The crystal structure of the monochloride has already been reported briefly;[4] the crystal contains dimeric units, each centred on a site of C_{2h} symmetry, and with no close contacts between dimers apparent. The structure is illustrated in Figure 4, and the structural parameters of the dimer are listed in Table 8. Comparison of bond lengths and angles in Table 3 and 8 shows that the change to trigonal-bipyramidal co-ordination at Si has been accompanied by significant increases in both the Si–N and the Si–Cl bond lengths. The change to tetrahedral co-ordination at N may be responsible for a slight increase in the C–N bond lengths. The 'additional' Si ··· N bonds in the ring are far too short (205.4 pm) to be regarded as simply close contacts between neighbouring molecules, but are still much longer than the shorter Si–N bonds in each half of the dimer, which at 181.3 pm are substantially longer than 'normal' Si–N bonds (*ca.* 165—170 pm).

In the crystal structure originally studied[4] the dimers of $SiH_2Cl(NMe_2)$ form a pseudo-face-centred lattice, and we have identified a second phase of this compound with a genuinely face-centred lattice. This form is orthorhombic, probable space group *Fmm*2, with $a = 687$, $b = 1\,005$, $c = 1\,550$ pm, $U = 1.070$ nm^3. The internal shape of the Pyrex tube appears to determine in which form the compound crystallises; we believe the second form to consist of dimers very similar to those found in the original form, as the *a* and *b* cell dimensions are very similar for the two forms. (In the original structure, $a = 676.6$, $b = 995.0$, and $c = 849.4$ pm.[4])

The crystal structure of the dichloride contains monomer units, whose bond length and angle parameters are given in Table 6 for comparison with the gas-phase electron diffraction results, and illustrated in Figure 3(*b*). It will be seen that they are very similar, showing that the molecular structure is not significantly affected by the change of phase. The only notable difference is in the conformations of the two methyl groups, which are now about 60° away from the positions found in the gas phase. The nitrogen atom is apparently perfectly planar, and the SiN torsion angle is only 3° away from the value of 90° corresponding to perfect alignment of the CNC plane with the plane bisecting the Cl–Si–Cl angle.

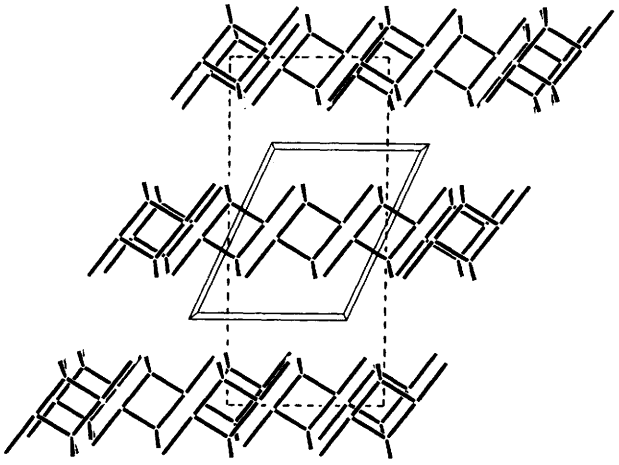

Figure 4. The crystal structure of $SiH_2Cl(NMe_2)$ at 116 K, showing the packing of dimers in planes. The structure is viewed down an axis parallel to *b*. The pseudo-orthorhombic face-centred cell is indicated by dotted lines, the true monoclinic cell by full lines

The two Si–Cl bond lengths are identical, as are the two CN bond lengths, though neither pair is required to be so crystallographically. The packing diagram (Figure 5) shows that the molecules appear to align themselves in chains parallel to *b*, but even the closest Si ··· Cl 'contact' is so remote (415 pm) that it affects neither the Si–Cl bond length nor the bond angles at Si significantly. It is perhaps best to regard this 'contact' as simply due to the packing of molecules without any very specific interactions, as the Si ··· Cl distance is greater than the sum of the van der Waals radii of the atoms. The closest intermolecular contacts are in fact Cl ··· H distances of 300 pm, just about equal to the sum of van der Waals radii. The resulting chain of molecules is rather different from those found in the simple halides MH_3X, where M = C, Si, or Ge, X = Cl;[12] or M = Si, X = F[13] or I,[14] as the Cl–Si ··· Cl angle here is only 158°, rather than almost 180° as in the simple halides, while the angle at Cl is much larger (126°) than in the simple chlorides.

Discussion

The structures reported here show some remarkable features, the most noteworthy of which is of course the formation of dimers in the crystalline phase of chloro(dimethylamino)silane.

This may be contrasted with the formation of a pentamer[15] in the crystalline phase of dimethylaminosilane itself. This also involves tetrahedral nitrogen and five-co-ordinate, trigonal-bipyramidal silicon, but the two nitrogen atoms occupy the axial positions, leaving the three hydrogen atoms in the equatorial positions. In the monochloride studied here, the chloride atom displaces one nitrogen from an axial to an equatorial position, forcing the two bonds to N from each Si to be almost orthogonal, and hence enforcing the formation of the observed four-membered ring of the dimer. We wondered whether a second chlorine would similarly displace the second nitrogen from the axial site, forcing a putative trimer of the dichloride to adopt a six-membered ring to accommodate 120° bond angles between Si–N bonds, both in the equatorial plane, but we found that no strong intermolecular bonding occurs, and the substance crystallises as monomeric units. We cannot therefore tell whether the fact that Cl takes an axial position in the dimer of the monochloride in preference to N is an expression of the superior 'apical preference' of Cl, of its higher electronegativity, of its greater size, or of the greater donor power of N (to Si), which makes the dimerisation through N favourable. Placing the two nitrogen atoms in axial sites would result in a chain polymer, such as is found for silyl cyanide, or a larger ring oligomer, such as the pentamer found for the parent dimethylaminosilane.

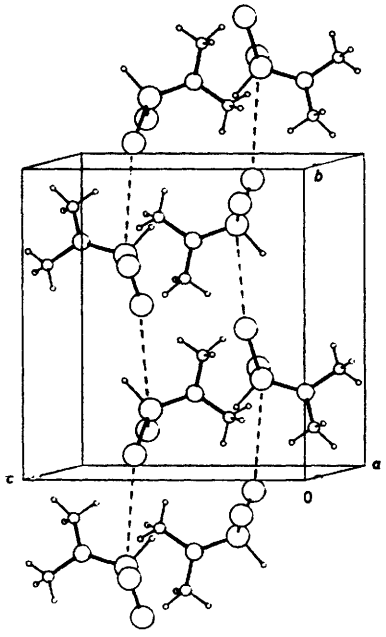

Figure 5. The crystal structure of $SiHCl_2(NMe_2)$ at 94 K, showing the loose association of monomers in chains parallel to the *b* axis. The Cl · · · Si 'contacts' between molecules are shown by dashed lines. The structure is viewed down an axis approximately perpendicular to *bc*

Another way to regard the dimer is as a frozen intermediate in an S_N2 reaction, in which a nitrogen atom attacks the Si of another molecule, displacing Cl; the position of Cl is then accounted for by the fact that Cl is a better leaving group than the dimethylamino group. As it has not been possible to make a full vibrational assignment for the dimer it is impossible to say what the stretching frequencies are for the 'short' and 'long' Si–N bonds in the dimer. In any case, such assignments are bound to be complicated by couplings between the SiN modes and the symmetric stretching modes of the dimethylamino groups, as in the monomer. Whatever the reason for its formation, the dimer seems to be the only stable species in the crystalline state; we have found no evidence for any crystal form not containing dimers, either by *X*-ray methods or by vibrational spectroscopy, and have shown[3] that the random solid formed by rapid condensation at very low temperatures from the gas phase, whose i.r. spectrum shows it to consist essentially of monomers, anneals smoothly and completely to the dimeric crystal form well below the melting point. On the other hand, we have found no evidence for the presence of dimers in the liquid, even at low temperatures just above the melting point, either from the Raman spectrum or from the n.m.r. spectrum.[3]

The dimer structure shown to be present in the monochloride is probably present in the crystalline states for the bromo- and iodo-analogues (judging from the changes in vibrational spectra on crystallisation), but we have not been able to obtain crystal structures for these substances. (Dimethylamino)fluorosilane, whose crystal structure would be of great interest, seems to be very unstable,[3] and we have been unable to prepare a sample pure enough for *X*-ray study.

The gas-phase structures are interesting for comparison with those of other dimethylaminosilanes which have been studied in recent years.[1,2,16] Table 9 shows some of the major structural parameters for a range of compounds having electronegative (halogen) or electron-donating (methyl) substituents at Si; the Si–N bond length is clearly decreased by halogen substitution, though all the methyl-substituted silyl amines have Si–N bond lengths very similar to that in dimethylaminosilane itself. In most cases the nitrogen atom appears to be slightly distorted from planarity, though both the most heavily methylated species and the most highly chlorinated species appear to have planar nitrogen.

The negative dip angles at nitrogen found here for the monohalogenosilanes are also interesting; they are consistently opposite in sign to those found for the analogous methyl-

Table 9. Structural parameters for some dimethylaminosilanes; electron diffraction r_a basis, distances in pm, angles in °

Compound	*r*(Si–N)	*r*(C–N)	CNC	SiNC	Sum of angles at N	Ref.
$SiH_3(NMe_2)$	171.5(4)	146.2(4)	111.1(12)	120.0(4)	351.1(20)	1
$SiH_2I(NMe_2)$	167.0(2)	146.8(3)	117.3(12)	119.1(4)	355.5(20)	This work
$SiH_2Br(NMe_2)$	168.4(4)	147.2(3)	109.8(14)	121.3(5)	352.5(23)	This work
$SiH_2Cl(NMe_2)$	168.7(2)	146.4(2)	115.1(6)	120.8(3)	356.8(11)	This work
$SiHCl_2(NMe_2)$	168.1(4)	146.4(3)	115.5(6)	122.1(3)	359.6(12)	This work
$SiCl_3(NMe_2)$	165.8(12)	144.8(12)	113(2)	123.5(2)	360 fixed	16
$SiF_3(NMe_2)$	165.6(15)	143.5(15)	120?	120?	360?	16
$SiH_2Me(NMe_2)$	171.5(6)	145.5(3)	112.7(8)	121.5(8)	355.6(15)	1
$SiHMe_2(NMe_2)$	171.9(5)	146.0(4)	113.7(15)	119.3(8)	352.4(18)	1
$SiMe_3(NMe_2)$	171.0(5)	146.2(4)	117.1(10)	121.4(5)	360 fixed	2

substituted silane,[1] though of similar magnitude. The methyl groups on nitrogen thus dip away from methyl on Si, but towards halogen. It seems most likely that this behaviour is due to the tendency for the nitrogen lone pair to avoid the halogen atom, but be attracted to the methyl group, rather then steric factors, which would be similar for both methyl and halogen substituents. It may be that steric effects are responsible for the exact apparent symmetry of the iodosilane, where the SiN torsion angle is zero, so that the large iodine atom is equidistant from the two methyl groups. The variations in CNC angles and C–N bond lengths seem to be rather random, and cannot be correlated with the substitution at Si; the values for the bromosilane reported here are particularly hard to explain. We can only suggest that this is a result of the poorer data for the bromide, due perhaps to the reaction noted between the compound and the emulsion; the *R* factors expressing the goodness of fit between the model and the observations are particularly high, presumably for this reason.

Finally, the results reported here show the importance of studying structures in more than one phase wherever possible, and of not assuming that effects found for one molecule will be operative in even closely related species.

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