Preparations, Properties, and Vibrational Spectra of some (Dimethylamino)halogenosilanes†

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We have prepared and characterised the new compounds $SiH_2Cl(NMe_2)$, $SiH_2Br(NMe_2)$, $SiH_2I(NMe_2)$, and $SiHCl_2(NMe_2)$. The vibrational spectra of the three (amino)monohalogenosilanes show dramatic changes on solidification, but those of the (amino)dichlorosilane are very similar in all three phases. These differences are discussed in the light of the formation of dimers in the crystalline solid of $SiH_2Cl(NMe_2)$, and the presence of discrete monomers in the crystal of $SiHCl_2(NMe_2)$. The n.m.r. spectra of the compounds, together with that of the monofluorosilane $SiH_2F(NMe_2)$, are reported and discussed briefly.

Difunctional silanes SiR_2X_2 are commonplace when R is an alkyl group, and are of immense importance as chain-forming precursors for silicone polymers, but comparatively few are known when R is H, despite the wealth of monofunctional silane chemistry that has been reported. We have recently begun to investigate the chemistry of compounds derived from dichlorosilane, SiH_2Cl_2, and have reported[1] the preparation and gas-phase structure of the first bis-ester of silane, $SiH_2(OCHO)_2$. We have also been studying the amines derived from dichlorosilane by reaction with dimethylamine, to form $SiH_2(NMe_2)_2$, and subsequent reactions of this compound. Here we report the preparation and spectroscopic characterisation of some (dimethylamino)halogenosilanes, $SiH_2X(NMe_2)$ (X = Cl, Br, or I) and the related dichloro(dimethylamino)silane. These compounds are of interest because the presence of the potential donor dimethylamino group and the potential acceptor silicon atom in the same molecule allows the formation of intermolecular complexes in some cases, but not in others, and we present spectroscopic evidence of such complex formation in the solid (amino)monohalogenosilanes, which has been confirmed by *X*-ray crystallography for the chloro compound. Some multinuclear n.m.r. studies are also reported, and these show no evidence for intermolecular association in the liquids, even at low temperatures; again, this is in accord with the Raman spectra, which show a sudden transition between monomer and dimer spectra on freezing. The *X*-ray studies, together with electron diffraction studies of the structures of the monomers in the gas phase, will be reported separately;[2] a preliminary communication has already appeared.[3]

A brief report of the formation of chloro(dimethylamino)silane appeared many years ago,[4] but no details of its properties other than an analysis for chlorine and a list of infrared frequencies with suggested assignments were given. It was formed by treating the rather involatile and inseparable decomposition products of the adduct formed between iodosilane and (dimethylamino)silane, presumably including (dimethylamino)iodosilane, with mercury(II) chloride. We have developed a specific synthesis for this material, and a general synthetic route for the formation of silicon-substituted (dimethylamino)silanes, which we have used for the formation of the bromo- and iodo-silyl species. The reactions of dichlorosilane with dimethylamine in the gas phase give bis(dimethylamino)silane or chloro(dimethylamino)silane, depending on the stoicheiometry of the reactants; equation (1) or (2). The

$$SiH_2Cl_2 + 4NHMe_2 \longrightarrow SiH_2(NMe_2)_2 + 2NH_2Me_2{}^+Cl^- \quad (1)$$

$$SiH_2Cl_2 + 2NHMe_2 \longrightarrow SiH_2Cl(NMe_2) + NH_2Me_2{}^+Cl^- \quad (2)$$

subsequent reaction of the bis(amino)silane with hydrogen halide HX (X = Br or I) affords a route to either the dihalogenosilane or the (dimethylamino)halogenosilane depending on the stoicheiometry; equation (3) or (4).

$$SiH_2(NMe_2)_2 + 4HX \longrightarrow SiH_2X_2 + 2NH_2Me_2{}^+X^- \quad (3)$$

$$SiH_2(NMe_2)_2 + 2HX \longrightarrow SiH_2X(NMe_2) + NH_2Me_2{}^+X^- \quad (4)$$

Experimental

All volatile silanes were handled in a vacuum system fitted with greased stop-cocks, and protected from contact with air and moisture. Compounds were separated by trap-to-trap distillation under low pressure using slush baths to maintain constant low temperatures, which were checked with an electrical resistance thermometer. Pressures were measured with a glass spiral gauge and mercury manometer. N.m.r. spectra were recorded on Bruker WH360, WP200, and WP80 spectrometers, using dilute solutions or neat liquids sealed in 5-mm glass tubes, with deuteriated solvent to provide a lock signal. I.r. spectra were recorded in 10-cm gas cells with KBr or CsI windows on Perkin-Elmer 598 spectrophotometers, as solid condensed from the gas phase on a CsI window cooled to a controlled low temperature by an Air Products CS-202 microrefrigerator operating down to 12 K using a Perkin-Elmer 225 spectrophotometer, or in a nitrogen matrix (1:500 to 1:1 000 matrix ratio) using the same apparatus. Raman spectra were recorded using a Cary 83 or a Spex Ramalab spectrometer with argon-ion laser excitation (488 or 514.5 nm) using samples held in glass capillaries.

Preparations.—(*i*) *Chloro(dimethylamino)silane.* Dichlorosilane (8 mmol) was treated with dimethylamine in the molar ratio of 1:2, using a two-bulb apparatus. The reaction involved the formation of one molar equivalent of dimethylammonium chloride as a white solid. The volatile products were removed from the bulb as soon as the addition was complete, and

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† *Non-S.I. unit employed:* Torr ≈ 133 Pa.

fractionated using a trap cooled to 209 K (chloroform slush), which retained most of the chloro(dimethylamino)silane, allowing any unreacted dichlorosilane or dimethylamine, together with more volatile impurities or decomposition products such as silane, chlorosilane, or disiloxane to pass through. Less volatile impurities, such as bis(dimethylamino)silane, were removed by passing the sample through a trap cooled to 227 K (chlorobenzene slush). Yields were very high, approaching 100% in some cases. The compound was a colourless liquid, melting point 193 K, vapour pressure at 273 K 46 Torr, molecular weight, by vapour density, 110.4 g (calc. 109.5 g). Spectroscopic characterisation is reported below.

A sample of chloro(dimethylamino)silane containing ^{15}N was prepared from ^{15}N-dimethylamine and dichlorosilane in a similar manner, using a smaller scale (*ca.* 1 mmol of amine); the yield was over 80%.

(*ii*) *Bromo(dimethylamino)silane and (dimethylamino)iodosilane.* Bromo(dimethylamino)silane was prepared by partial cleavage of the Si–N bonds in bis(dimethylamino)silane by HBr in the gas phase; the iodosilane was prepared by an analogous reaction using HI. The bis(dimethylamino)silane was prepared by the same route as the chloro(dimethylamino)silane above, using a four-fold ratio of dimethylamine to dichlorosilane. It was essential to remove the volatile product from the two-bulb reaction vessel and wash the dimethylammonium chloride out with dilute acid before the second step, as ready halide exchange was found to occur, bromo- and iodo-silanes being readily converted to chlorosilanes by contact with solid chlorides.

Bromo(dimethylamino)silane is a colourless liquid at room temperature, but sublimes in a vacuum system forming long needles. It was retained in a trap cooled to 227 K, but passed a trap cooled to 250 K. The vapour pressure at 273 K was 16 Torr, and the molecular weight, by vapour density, 152 g (calc. 154 g).

(Dimethylamino)iodosilane is a white solid at room temperature, subliming in the vacuum system; it is retained in a trap cooled to 227 K. Warming the sample above room temperature in a sealed capillary led to melting with some decomposition, and a reproducible melting point could not be obtained. The vapour pressure was low, and neither this nor the vapour density was measured accurately.

It was noted that the reaction between HI and bis(dimethylamino)silane was not quantitative; even with excess of HI over the stoicheiometric 2:1 ratio some of the starting bis-amine remained, and it was difficult to separate this from the product, (dimethylamino)iodosilane, by fractionation. It is suggested that intermolecular association, as has been shown[4] to occur between iodosilane itself and (dimethylamino)silane, and as is shown here to occur in solid (dimethylamino)iodosilane, also occurs between the bis(dimethylamino)silane, the (dimethylamino)iodosilane, and any other iodosilane(s) and aminosilane(s) present or formed in the reaction. A spectroscopically pure sample of the (dimethylamino)iodosilane was eventually produced by careful adjustment of the reacting ratio and exhaustive fractional condensation.

(*iii*) *Dichloro(dimethylamino)silane.* This was prepared from trichlorosilane (8.5 mmol) and 2 equivalents of dimethylamine in a two-bulb apparatus, volumes 250 cm^3 and 1 000 cm^3; the amine, in the smaller bulb, was allowed to mix with the trichlorosilane in the larger bulb in small pulses, so that local excesses of amine were avoided. Yields were typically high, over 90% in most attempts. Fractionation using a trap at 209 K allowed the collection of pure dichloro(dimethylamino)silane.

Dichloro(dimethylamino)silane is a colourless liquid at room temperature, melting point 165 K, vapour pressure at 271.4 K 13 Torr.

(*iv*) *(Dimethylamino)fluorosilane.* Several possible routes to this compound were investigated. The reaction of bromo(dimethylamino)silane with SbF_3 gave less than 50% yield, after fractionation using traps at 177 and 153 K, of a colourless liquid whose n.m.r. spectra (see below) were consistent with its formulation as (dimethylamino)fluorosilane, but the sample slowly decomposed before physical characterisation. The reaction of chloro(dimethylamino)silane with GeH_3F appeared to give the same substance initially, but before it could be separated from the other product, chlorogermane, it decomposed to give SiH_2F_2. Reaction of bis(dimethylamino)silane with BF_3 gave a white solid adduct initially which decomposed at room temperature to give more of the same compound, but again it decomposed before full characterisation. The gas-phase i.r. spectrum and n.m.r. spectra were recorded, and are discussed further below.

Results and Discussion

N.M.R. Spectra.—Proton, ^{13}C, and ^{29}Si n.m.r. spectra were recorded for the compounds, and the results are shown in Table 1, together with the ^{19}F spectrum of the substance believed to be (dimethylamino)fluorosilane. [$^2H_8$]Toluene was used as solvent to allow work at low temperatures, the solvent (methyl) ^2D peak serving as a lock signal and internal reference.

The parameters of the dimethylamino group are fairly constant, varying only slightly with the other substituents on silicon, but the Si chemical shift is, as expected, more variable, though there seems to be no consistent trend in the values for the four monohalides, and the shift for the dichlorosilane is very similar to that for the monochlorosilane. This parallels the changes observed for the simple halogenosilanes SiH_nX_{4-n}, where X is halogen and n = 1, 2, or 3. In particular, the more negative chemical shift when Si is bonded to iodine appears in this context to be due to a smaller positive change in shift for the heavy halogen (regarded as substituted for H) than for the

Table 1. N.m.r. parameters[a]

Compound	δ H(Si)[b]	δ H(C)[b]	δ ^{29}Si[c]	δ ^{13}C[d]	$^1J_{CH}$	$^1J_{SiH}$	$^3J_{CH}$	$^3J_{SiH}$
$SiH_2F(NMe_2)$[e]	4.39	2.24	−22.57	36.94	133	249.9	3	
$SiH_2Cl(NMe_2)$[f]	4.78	2.17	−20.97	36.93	135.8	259.0	4	5
$SiH_2Br(NMe_2)$	4.85	2.12	−27.62	39.06	135.2	263.0		
$SiH_2I(NMe_2)$	4.84	2.01	−47.2	37.4	135.0	262.8	5	
$SiHCl_2(NMe_2)$	5.27	2.18	−21.75	34.46	136.0	315.8	3.5	

[a] All spectra were recorded using dilute solutions in [$^2H_8$]toluene, and used the methyl ^2D signal as lock and internal reference. Chemical shifts (in p.p.m.) were referred to $SiMe_4$ (^1H, ^{13}C, and ^{29}Si), to CCl_3F (^{19}F), or to nitromethane (^{15}N); positive chemical shifts are to high frequency. Only the magnitudes of coupling constants (in Hz) are given; absolute or relative signs were not determined. [b] ^1H Spectra recorded at 80.13 (spectrometer WP80) or 200.13 MHz (WP200). [c] ^{29}Si spectra recorded at 39.76 MHz (WP200). [d] ^{13}C Spectra recorded at 50.32 MHz (WP200). [e] ^{19}F Spectra recorded at 75.39 MHz (WP80). δ $^{19}F = -144.3$ p.p.m., $^1J_{SiF} = 308$, $^2J_{HF} = 69.5$, $^3J_{CF} = 2.8$, $^4J_{HF} = 3.37$ Hz. [f] ^{15}N Spectra recorded at 36.51 MHz (WH360). δ $^{15}N = -366.67$ p.p.m., $^1J_{SiN} = 22.56$, $^2J_{HSiN} = 7.26$, $^2J_{HCN} < 0.25$ Hz.

lighter halogens, F and Cl. The proton chemical shifts change with change of halogen substituent in the opposite direction to that observed for the methylhalogenosilanes,[5] both for the hydrogen atoms bound to Si and those bound to C, but the one-bond SiH coupling constants change in the same way as found for the methylhalogenosilanes. The values of $^1J_{SiH}$ are smaller for the four amino monohalides than for dihalogenosilanes (around 280 Hz), and larger, as expected, for the dichlorosilane, though not as large as for trichlorosilane (363 Hz). The long-range coupling observed in the ^{13}C spectra, labelled $^3J_{CH}$ in Table 1, is probably due to coupling to the protons of the second methyl group in most cases, as a quartet splitting of this

Table 2. Vibrational spectra of $SiH_2X(NMe_2)$ monomers

Compound	$SiH_2F(NMe_2)$	$SiH_2Cl(^{15}NMe_2)$	$SiH_2Cl(NMe_2)$			$SiH_2Br(NMe_2)$			$SiH_2I(NMe_2)$
Sample	Gas	Gas	Gas	Matrix	Liquid	Gas	Matrix	Liquid	Gas
Technique	I.r.	I.r.	I.r.	I.r.	Raman	I.r.	I.r.	Raman	I.r.
Suggested assignment									
ν(CH)				2 982					
	2 970m	2 970	2 976m	2 974	2 966w, p	2 974	2 970		2 968
				2 926	2 936m, p	2 917	2 942		2 915
	2 900s	2 904	2 904s	2 900w	2 900m, p	2 907m	2 908m		2 903m
		2 888	2 894m	2 887		2 889	2 899		2 890
							2 888		
	2 870	2 868	2 867m	2 858	2 852m, p	2 862	2 857		2 859
	2 810m	2 812	2 816m	2 817	2 805m, p	2 815	2 815		2 811
				2 811					
ν(SiH)				2 233			2 229		
				2 227 }w			2 225		
	2 200vs	2 203	2 206vs	2 224	2 191s, p	2 206	2 210	2 190	2 198vs
				2 215 }m		2 193 }s	2 205 }s		
				2 209					
				2 197 }w			2 196		
$\delta_{asym.}(CH_3)$			1 500w				1 490		1 503
			1 494w	1 491		1 486	1 487	1 486w	1 494
	1 482	1 481	1 485w		1 485w, dp	1 478	1 469		1 483
	1 466	1 469	1 469w	1 472		1 470	1 465		1 469
		1 463	1 464w	1 470		1 463	1 452		1 462
$\delta_{sym.}(CH_3)$	1 453	1 455	1 455w	1 450	1 422m, dp?	1 457	1 450	1 440m	1 452
						1 453	1 448		
$\nu_{sym.}(NC_2)$				1 316			1 311		
				1 311 }w			1 307		
	1 309s	1 291	1 303s	1 304	1 302m, p	1 305m	1 298	1 297w	1 301
				1 300 }m			1 224 }m		
$\nu_{asym.}(NC_2)$	1 188s	1 116	1 187s	1 184m		1 185m	1 182		1 184
				1 178s			1 174 }s		
$\rho(CH_3)$ *a″*	1 076w	1 072	1 076w	1 073m	1 074vw, dp	1 076w	1 070		1 075
				1 069	1 067				
$\rho(CH_3)$ *a′*				1 010s					
	1 009s	1 001	1 009s	1 005s	1 008w, dp	1 010s	1 007s	1 000w	1 005
				996w			999s		
$\delta_{sym.}(SiH_2)$	940vs	937	939s	929s	929m, p	930s	923s	918w	925s
$\delta_{wag.}(SiH_2)$	940vs	895	894vs	900s	887m, p	875vs	870	860w	852vs
				888vw			865 }vs		
$\tau(SiH_2)$	750vw	—	769vw	730vw	772m, dp?	760w	759	755w	753
							737 }vw		
ν(SiN)	676	690	689m	688	689vs, p	686m	686m	681s	684
				687 }m					
$\rho(SiH_2)$		627	625m	632	625w, p	603m	604	652w	574
				623 }m			598 }m		
ν(SiX)	855	519	519s	501s	497vs, p	419s	400s	397vs	362m
δ(CNC)	380vw		371vw	367vw	370m, p		364w	368w	
δ(NSiX), *etc.*	425w		298vw	309	300m, p			268w	
	315vw			305	200w				
					110m, dp				

w = Weak, m = medium, s = strong, v = very; p = polarised, dp = depolarised.

magnitude can be discerned, but may in some cases be due to coupling to the two protons on Si. In either case, the corresponding peaks in the proton spectra, where lower noise levels are found, are close satellites of very strong signals, and cannot be separated from them. The three-bond coupling to Si, observed only in the neat liquid sample of the monochloride, is clearly due to the six equivalent methyl protons, giving a seven-line pattern.

The ^{15}N spectrum of the labelled chloro-compound shows clearly that the Si–N bond is not labile on the n.m.r. time-scale, as fully-resolved coupling to Si and to protons on Si are observed. Interestingly, the coupling to the methyl protons appears to be very small, as found for other methylamines. In the non-labelled materials, there were no signs of discrete patterns in any of the spectra due to coupling to ^{14}N, but the lines of the amino compounds in the proton spectra were noticeably broader than those assigned to substances not containing nitrogen. This broadening was also noted in the ^{29}Si spectrum of the neat liquid chloride, where the line due to the amine was some 10 Hz wide, even with all proton couplings removed, at room temperature. These effects may well be due to the fast relaxation of the quadrupolar ^{14}N nucleus, as the line-width decreased as the temperature was lowered (see below).

In view of the possibility of intermolecular association in the monohalogenosilanes, a tube containing pure chloro(dimethylamino)silane was prepared, with a capillary insert containing [^{2}H$_6$]acetone as lock; the ^{29}Si n.m.r. spectrum, which was expected to be most sensitive to additional co-ordination at Si, was studied at low temperatures, which were expected to favour the association. The signal due to the chlorosilane showed no changes attributable to the formation of additional bonds to Si, though traces of disproportionation products [probably SiH_3Cl and $SiHCl(NMe_2)_2$] were found after the tube had been left at room temperature for a short period.

I.r. and Raman Spectra.—Table 2 gives a list of the bands observed for gaseous, liquid, or matrix-isolated samples of the compounds, which we believe to correspond to monomeric

Table 3. I.r. and Raman spectra of annealed solid phases (n.r. = region not recorded)

$SiH_2Cl(NMe_2)$		$SiH_2Cl(^{15}NMe_2)$	$SiH_2Br(NMe_2)$		$SiH_2I(NMe_2)$		
I.r.	Raman	I.r.	I.r.	Raman	I.r.	Raman	Suggested assignment
2 970w	2 996m 2 939m	2 970w	2 969w	2 990w	2 960w		ν(CH)
2 900w		2 900w	2 900w		2 900w	n.r.	
2 847w	2 853w	2 848w	2 844w	2 842	2 840w		
2 802w	2 801w	2 801w	2 802w		2 796w		
2 222m 2 197m	2 206s	n.r.	2 231m 2 189m	2 202m	2 190s	2 216s	ν(SiH)
1 469m	1 477m	1 470m	1 470m	1 471m	1 470m	1 470m	$\delta_{asym.}(CH_3)$
1 458m	1 446m	1 460m	1 458m	1 442w	1 460m	1 454w	
	1 436w		1 432w	1 427w	1 432w	1 440w	$\delta_{sym.}(CH_3)$
			1 405w			1 429m	
						1 398w	
1 305w	1 311vw	1 310w	1 306vw		1 310		$\nu_{sym.}(NC_2)$, $\nu_{asym.}(NC_2)$
1 241w	1 232w	1 232w	1 241w		1 240w		
1 135m		1 123m	1 135m		1 133m		$\rho(CH_3)$
1 070w	1 068w	n.r.	1 090w	1 100w	1 089vs	1 096w	
1 037m	1 023w	1 016s	1 032m	1 014s	1 013s	1 013w	
1 020s	1 018w		989vs	991w			
				980w			
970w	976w	970w	943w	948w	948m	942w	$\delta_{sym.}(SiH_2)$
908s	929m	900s	906vs	917vs	904vs	904w	$\delta_{wag.}(SiH_2)$
			860m	835m	879m		$\nu(Si_2N_2)$ ring
814s		814vs	802s	794m	808s		
	796w			777s		735w	
			729w	711w			
						683w	$\nu(Si_2N_2)$ ring
				695w			
624m		620m	619s	649m	611s		
	603s					595vs	
				596vs			
565w		$\left.\begin{matrix}562\\550\end{matrix}\right\}$w	557w				
	501m			495s		490w	ν(SiX)
480s		476s	482vs		480s		δ(CNC), ring deformations, *etc.*
				437w			
376s		376s	368s		370s		
	386m			378m		380m	
323s	326s	325s	291s	292vs	318m	293vs	
	271m		250s	262s	290m	274m	
					262m		
	208s						Deformations at Si, ring torsion, lattice modes
	179s			168m		153m	
				150m		147m	
	117m						
	58s						

Table 4. I.r. and Raman spectra of $SiHCl_2(NMe_2)$

Gas i.r.	Solid i.r.	Solid Raman	Liquid Raman	Suggested assignment
2 970m	2 972	2 978w	2 968w	ν(CH)
2 911s	2 918	2 931w	2 929w	
	2 900m	2 903w		
2 865m	2 851	2 858w	2 856m	
2 818m	2 809	2 810m	2 811m	
2 241s	2 244s	2 243vs	2 236vs	ν(SiH)
1 487	1 486m	1 488m	1 487m	$\delta_{asym.}(CH_3)$
1 465w	1 469w			
1 456	1 445m	1 441m	1 443ms	$\delta_{sym.}(CH_3)$
		1 433mw	1 419mw	
		1 412mw		
1 309s	1 314vs	1 310mw	1 307m	$\rho(CH_3)$ *a′*
1 187s	1 183s			
	1 171s	1 149mw	1 146w, dp	$\rho(CH_3)$ *a″*
1 080m	1 074m	1 079mw	1 075w, dp	$\nu_{asym.}(NC_2)$
1 006vs	1 006vs	1 006m	1 004m, dp?	$\nu_{sym.}(NC_2)$
847vs	834vs	837ms	842m, dp?	δ(SiH) *a′*
808vs	782vs	776vs	792m, dp	δ(SiH) *a″*
702m	699s	701m	700s, p	ν(SiN)
573vs	537vs	517m	560m, dp	$\nu_{asym.}(SiCl_2)$
520s	502vs	504vs	503s, p	$\nu_{sym.}(SiCl_2)$
430vw	451vw			
402vw	381m			
	329w	330s	326vs, p	δ(CNC)
303vvw	291m	285m	297m, dp	
		264m		
		196s	188s	Deformations at Si, torsions, *etc.*
		170m	175s	
		152s	134m	
			110m	

materials. An assignment is suggested, based on the bands found for other di-substituted silanes,[6] (dimethylamino)silanes,[7] and halogenosilanes. The assignments for the chloro(dimethylamino)silane were also based on the isotopic shifts observed between the ^{15}N and normal species, which confirmed that several bands above 1 000 cm^{-1} showed significant isotopic shifts, but that no bands in the 1 000—400 cm^{-1} range shifted by more than 2 cm^{-1}. This, at first sight puzzling, observation is consistent with the suggestion that the two CN stretches couple to give symmetric and antisymmetric components, of which the symmetric mode itself couples with the SiN stretch (expected at lower frequency), resulting in two 'symmetric' modes, one of which, at higher frequency, involves significant motion of the nitrogen atom and hence shows a nitrogen isotopic shift, while the other, at lower frequency, around 700 cm^{-1}, involves a symmetric displacement of the Si atom and the two methyl groups about the almost stationary nitrogen and shows no such shift. Assignments in the region from 1 000 to 1 350 cm^{-1} are complicated by the expected presence of four methyl rocking modes in this region, as well as the NC_2 stretches. In themselves, the assignments are otherwise unremarkable, and we shall not discuss them further. The i.r. spectra of solid samples condensed from the gas phase at temperatures well below the melting points showed bands at similar frequencies, and we believe these samples to consist largely of monomeric molecules. The spectra of the monochloro- and monobromo-silanes changed progressively on annealing, as illustrated in the Figure; fully-annealed samples were only obtained by warming to well over 100 K, but features attributable to the 'annealed' molecular species (believed to be the dimer) began to appear even at quite low temperatures.

In Table 3 we list the bands found in annealed solid samples of the three monohalogenosilanes (chloro, bromo, and iodo). Comparison with the data in Table 2 shows that above 1 300 cm^{-1} there is little change on solidification, but below this frequency several bands shift or split dramatically. In particular, the bands assigned to the SiN stretch (probably coupled to the symmetric CN stretch of the dimethylamino group, see above) near 700 cm^{-1} for gas or liquid samples vanish, to be replaced by bands near 800 and 600 cm^{-1} in the solids. We take this as showing that a dramatic change in the molecular structure occurs on crystallization; indeed, it was this change in the spectra that first alerted us to the possibility that the molecular structure might be different in the crystal, and prompted the investigation of the crystal structure. In view of the evidence of dimer formation in the chloro-compound from *X*-ray crystallography[2,3] we suggest that a similar dimerisation is involved for the bromo- and iodo-compounds as well. No such change is observed on solidification in the spectra of the dichloro(dimethylamino)silane (Table 4), and this is consistent with *X*-ray evidence[2] that this compound crystallizes as monomeric units.

The changes in other regions of the spectra of the monohalogeno-compounds are less dramatic, but can be explained as consequences of the change in co-ordination at Si from tetrahedral to trigonal bipyramidal. The strong Raman band near 500 cm^{-1} in the liquid chloride, assigned to the SiCl stretching mode of the monomer, is much weaker in the crystal. New bands below 400 cm^{-1}, strong in both i.r. and Raman, are probably due to deformations of the Si_2N_2 ring. A full assignment of the spectra of the dimers is not practicable, even with the spectra of several related compounds, but it is worth pointing out that in the 300—850 cm^{-1} region many bands appear as pairs, one component active only in the i.r., the other

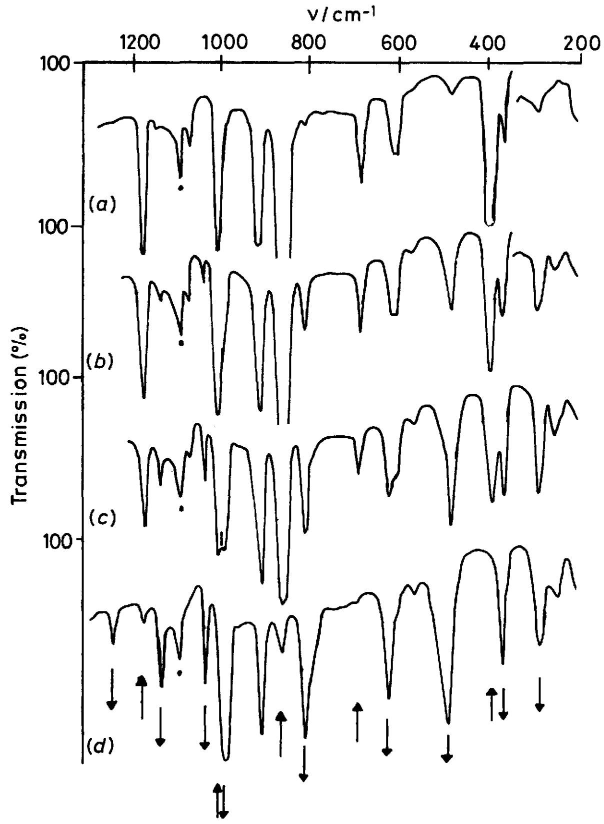

Figure. I.r. spectra of solid $SiH_2Br(NMe_2)$ at 17 K after annealing to the temperatures (*a*) 17, (*b*) 40, (*c*) 57, and (*d*) 135 K. Note the decrease in intensity of those bands marked by an arrow pointing upwards, which are assigned to the monomer, and the increase in intensity of those bands marked by an arrow pointing downwards, assigned to the dimer, as the annealing temperature rises. The peak at 1 070 cm^{-1}, marked ●, is due to bisulphate ions on the cell windows

only in the Raman, as expected from the centrosymmetric dimer found in the solid chloride. In the solid dichlorosilane (Table 4), one band, at 537 cm^{-1} in the i.r., has its Raman counterpart slightly displaced to 517 cm^{-1}, again suggesting a pair of molecules related by an inversion centre, as found in the crystal structure. The SiCl stretching modes in this case are distinctly lower in frequency in the solid than in the gas, which suggests association through chloride bridges rather than nitrogen bridges; again, this is confirmed by the crystal structure, which shows no sign of Si • • • N contacts between molecules, but has rather long Si • • • Cl contacts.

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