

# Bis(chloromethylsilyl)amine and bis(chloromethylsilyl)methylamine; preparation, reactivity and spectroscopic studies of their stereoisomers and conformers‡

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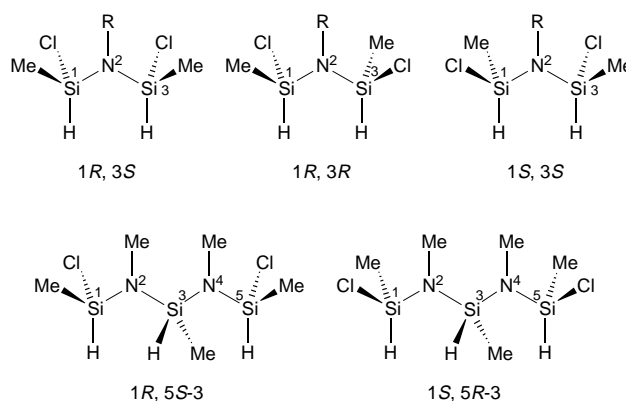
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The compounds  $\text{NH}(\text{SiHMeCl})_2$  **1** and  $\text{NMe}(\text{SiHMeCl})_2$  **2** have been prepared by treating  $\text{SiHMeCl}_2$  with  $\text{CaCl}_2 \cdot 8\text{NH}_3$  and  $\text{NH}_2\text{Me}$  respectively. Each was characterised by elemental analysis, mass spectrometry, NMR and IR spectroscopy. Dipole moments were also measured. The NMR spectra indicate that both compounds form 1 : 1 mixtures of the *rac* and *meso* diastereomers, their abundances corresponding to a statistically controlled synthetic pathway. The NMR and mass spectra also show that 1,5-dichloro-1,2,3,4,5-pentamethyltrisilazane,  $\text{SiHMe}[\text{NMe}(\text{SiHMeCl})_2]$  **3**, which is formed as a side product in the synthesis of **2**, also consists of two diastereomers. Variable-temperature  $^1\text{H}$  NMR spectra of  $\text{NH}(\text{SiHMeCl})_2$  indicate participation of H(N) in hydrogen bonding. The compound is decomposed by heat and reacts with pyridine to form  $\text{NH}_4\text{Cl}$ ,  $\text{SiHMeCl}_2$  and polysilazanes, whereas  $\text{NMe}(\text{SiHMeCl})_2$  shows only slight decomposition up to 80 °C and does not react with pyridine. Infrared spectra in the  $\nu(\text{SiH})$  region are interpreted in terms of the results of *ab initio* calculations of frequency, intensity and conformer abundance. The two bands near  $2200\text{ cm}^{-1}$  in the spectrum of **2** have their origin in two effects: different orientations of the Si–H bonds relative to the Si–N–Si plane in several conformers and an unprecedented strong dipole–dipole coupling between the two Si–H bond stretching motions in situations where the bonds are roughly parallel. The absence of such an observed splitting for **1** is likely to be due in part to signal averaging during a free internal rotation. Significant couplings are also calculated to occur between Si–Cl bond-stretching motions, whose source must be different from that for the Si–H bond stretches.

Substituted disilylamines have been the subject of a number of recent chemical and structural investigations.<sup>1–4</sup> To date, the species studied for structural purposes have involved symmetrically substituted silyl groups, *viz.*  $\text{NH}(\text{SiHMe}_2)_2$ ,<sup>1</sup>  $\text{NMe}(\text{SiHMe}_2)_2$ ,<sup>2</sup>  $\text{NMe}(\text{SiH}_2\text{Me})_2$ ,<sup>2</sup>  $\text{NH}(\text{SiHCl}_2)_2$ <sup>3</sup> and  $\text{NMe}(\text{SiHCl}_2)_2$ ,<sup>3</sup> where the interest has been mainly in the conformations adopted following the substitution of hydrogen by chlorine or methyl groups.

Asymmetrically substituted silylamines have the additional interest as being potential precursors for the synthesis of optically active polysilylazanes, inorganic equivalents of peptides and proteins, and for SiN-based ceramics bearing chiral and functionalised silicon surface groups. The present investigation of two such disilylamines, **1** and **2**, was designed to discover which of the possible stereoisomers of the compounds were present and to study their chemical, spectroscopic and structural properties. As shown in Scheme 1, both compounds can give rise to two diastereoisomeric forms, the optically inactive isomer with the 1*S*,3*R* (= 1*R*,3*S*) configuration, denoted *meso*-**1** and *meso*-**2**, and a racemic mixture of the two optically active forms with 1*S*,3*S* and 1*R*,3*R* configurations, denoted *rac*-**1** and *rac*-**2**. While this work was in progress, the synthesis of **1** and **2** was reported, together with some infrared and NMR data.<sup>5</sup>

In the present paper we describe new low-temperature methods of preparation of the two compounds, explore further their chemical properties and present spectroscopic and dipole moment evidence bearing on the nature of the conformers present. In the accompanying paper,<sup>4</sup> gas-phase electron diffraction and *ab initio* studies are reported. These include geometry and



**Scheme 1** Structural formulae of bis(chloromethylsilyl)amine **1** ( $\text{R} = \text{H}$ ), bis(chloromethylsilyl)methylamine **2** ( $\text{R} = \text{Me}$ ) and 1,5-dichloro-1,2,3,4,5-pentamethyltrisilazane **3**

energy calculations at the MP2 level and SCF calculations of force constants, vibration frequency and infrared intensity. Results from the latter SCF calculations are used here in the interpretation of the infrared spectra, which focuses mainly on the bands appearing in the Si–H stretching region.

Previous infrared studies<sup>6–8</sup> of the Si–H stretching regions in silylamines and ethers have shown that isolated SiH stretching frequencies,  $\nu_{\text{SiH}}(\text{SiH})$ , measured for preference in partially deuterated species, are sensitive to the orientation of the Si–H bond with respect to the skeletal plane of the molecule and this information may be used to deduce the conformation(s) present in a sample.<sup>7</sup> They also enable simple rules for the lowering of  $\nu_{\text{SiH}}(\text{SiH})$  by methyl or its raising by halogen substitution to be deduced, which are relevant when conformational analysis is attempted.

Although spectra of partially deuterated species were not

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<sup>‡</sup> Non-SI units employed: Torr  $\approx 133\text{ Pa}$ , D  $\approx 3.33 \times 10^{-30}\text{ C m}$ .

**Table 1** Proton,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectral data for compounds **1**, **2** and **3**. Two entries denote values for different diastereomers

	<b>1</b>	<b>2</b>	<b>3</b>
$\delta$			
$\text{H}_3\text{C}_{\text{Si}}$	0.60	0.61	0.27, <sup>a</sup> 0.50, <sup>b</sup> 0.51 <sup>b</sup>
$\text{H}_3\text{C}_{\text{N}}$	—	2.67, 2.68	2.51
$\text{H}_{\text{N}}$	1.90	—	—
$\text{H}_{\text{Si}}$	5.12, 5.14	5.12	4.51, <sup>a</sup> 5.02 <sup>b</sup>
$\text{H}_3\text{C}_{\text{Si}}$	2.28, 2.34	1.00, 1.04	−2.76, <sup>a</sup> 1.06, <sup>b</sup> 1.12 <sup>b</sup>
$\text{H}_3\text{C}_{\text{N}}$	—	29.3, 29.6	29.18, 29.32
Si	−5.33	−0.85	—
$^1J(\text{H}^{1\text{H}}\text{--}^{29}\text{Si})/\text{Hz}$	253	254	227, <sup>a</sup> 256 <sup>b</sup>
$^1J(\text{H}^{1\text{H}}\text{--}^{13}\text{C}_{\text{N}})/\text{Hz}$	—	137	140
$^1J(\text{H}^{1\text{H}}\text{--}^{13}\text{C}_{\text{Si}})/\text{Hz}$	122.5	123.0	—
$^3J(\text{H}_{\text{C}}\text{--}^1\text{H}_{\text{Si}})/\text{Hz}$	2.44	2.63	2.79, <sup>a</sup> 2.18, <sup>b</sup> 2.52 <sup>b</sup>
$^3J(\text{H}_{\text{N}}\text{--}^1\text{H}_{\text{Si}})/\text{Hz}$	1.60	—	—

<sup>a</sup> Signals originate from central ( $\text{Si}^3$ ) SiHMe group. <sup>b</sup> Signals originate from terminal ( $\text{Si}^1$ ,  $\text{Si}^5$ ) SiHMe groups.

**Table 2** Proton NMR shifts and  $^1J(\text{H}^{1\text{H}}\text{--}^{29}\text{Si})$  coupling constants for some hydridosilanes and silylamines

Compound	$^1J(\text{H}^{1\text{H}}\text{--}^{29}\text{Si})/\text{Hz}$	$\delta(\text{H}_{\text{Si}})$	Ref.
$\text{SiHF}_3$	381	4.51	10
$\text{SiHCl}_3$	364	6.12	11
$\text{SiHBr}_3$	360	6.44	11
$\text{NH}(\text{SiHCl}_2)_2$	336	5.76	9
$\text{NMe}(\text{SiHCl}_2)_2$	327	5.71	9
$\text{SiH}_3$	325	4.49	11
$\text{SiHMeCl}_2$	279	5.58	12
$\text{SiHMe}_2\text{Cl}$	—	4.87	12
$\text{SiHMe}_3$	182	3.85	12

obtained in this work, a detailed study of the vibrational properties of the molecules concerned has been made using the aforementioned *ab initio* calculations, whereby valence force constants for the individual bonds and their stretch–stretch interactions have been obtained as well as frequencies for the partially deuterated species. These reveal unexpected couplings between the bond stretching motions, a factor which must be considered if conclusions about the conformations present are to be drawn.

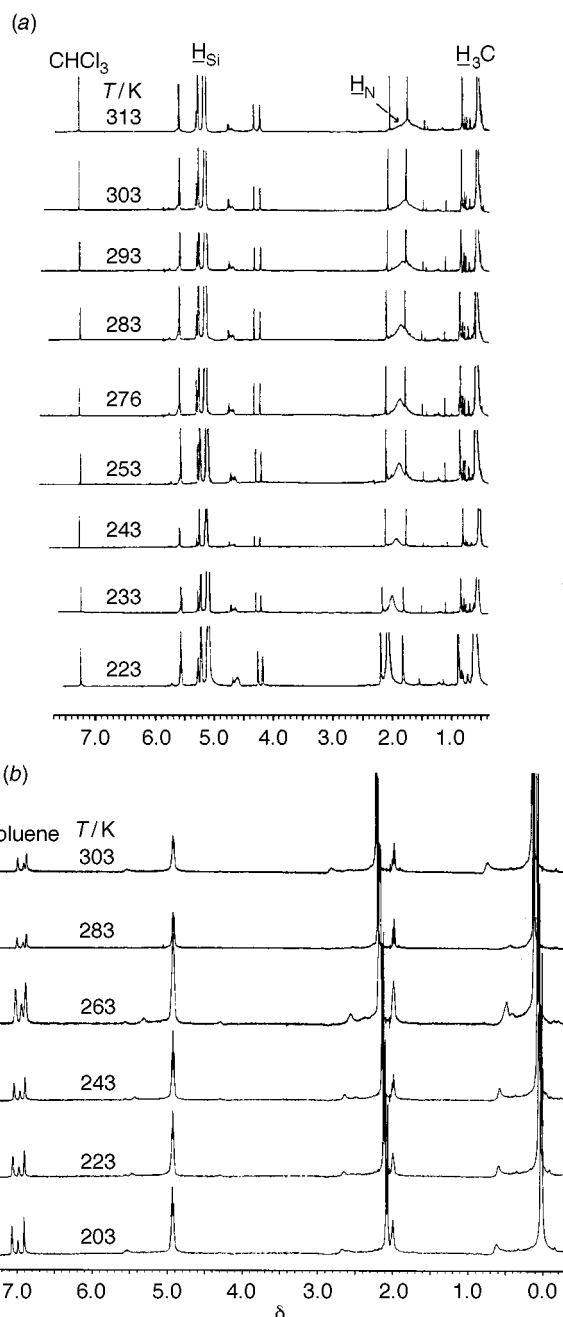
## Results and Discussion

### NMR studies

The data obtained are listed in Table 1. The resonances can be satisfactorily assigned by comparison with the spectra of the related molecules  $\text{NH}(\text{SiHCl}_2)_2$ ,<sup>9</sup>  $\text{NMe}(\text{SiHCl}_2)_2$ ,<sup>9</sup>  $\text{SiHX}_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$  or  $\text{Me}$ ),<sup>10–12</sup>  $\text{SiHMe}_2\text{Cl}$  and  $\text{SiHMeCl}_2$ ,<sup>12</sup> data for which are given in Table 2. Values of  $\delta\text{H}(\text{Si})$  and  $^1J(\text{H}^{1\text{H}}\text{--}^{29}\text{Si})$  are in agreement with the trends discerned for the compounds in Table 2.

The origin of some of the signal splittings in the spectra of compounds **1** and **2** does not lie in spin–spin couplings but in distinct differences in chemical shift. This was shown by recording spectra at different field strengths. Variable-temperature  $^1\text{H}$

§ The magnitude of  $^1J(\text{H}^{1\text{H}}\text{--}^{29}\text{Si})$  is a good indicator for the withdrawal of electron density by the three other ligands in monohydridosilanes. Table 2 shows that high values correlate with very electronegative substituents. The chemical shift of the H atom directly bound to the Si atom,  $\delta\text{H}(\text{Si})$ , does not reflect the electronegativity in every case, as can be seen by comparison of  $\text{SiHF}_3$  and  $\text{SiH}_3$ . However, if only Cl,  $\text{NR}_2$  and Me are considered as ligands,  $\delta\text{H}(\text{Si})$  decreases with decreasing electron-withdrawing force. The values of  $\delta\text{H}(\text{Si})$  and  $^1J(\text{H}^{1\text{H}}\text{--}^{29}\text{Si})$  of **1–3** (see Table 1) fit in very well in the series, **3** clearly showing the different  $\delta\text{H}(\text{Si})$  values for  $\text{SiHMe}[\text{NMe}(\text{SiHMeCl})_2]$  (4.51) and  $\text{SiHMe}[\text{NMe}(\text{SiHMeCl})_2]$  (5.02).

**Fig. 1** Variable-temperature  $^1\text{H}$  NMR spectra of (a) compound **1** in  $\text{CDCl}_3$ , (b) **2** in  $[\text{H}_8]\text{toluene}$ 

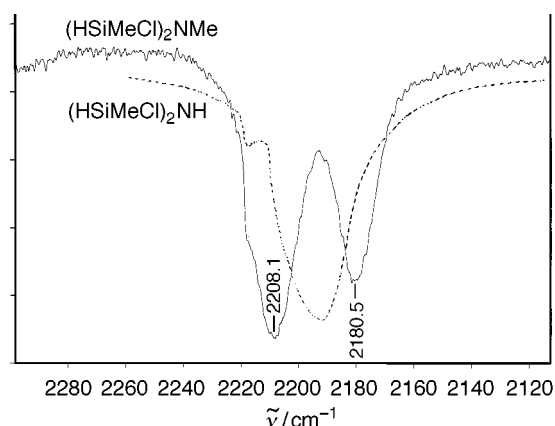
NMR spectra (Fig. 1) showed no coalescence of peaks and no variation in intensity ratios. [The most striking effect of changing temperature seen in Fig. 1 is that on  $\delta\text{H}(\text{N})$  for compound **1**. The high-field shift with rise in temperature indicates participation of the N–H bond in a hydrogen bridge.<sup>9</sup>] Furthermore, internal rotation about the Si–N bonds is usually sufficiently rapid to cause averaging of the NMR signals of different conformers.

All these considerations point to the presence in solutions of compounds **1** and **2** of chemically similar, but non-equivalent species in equal abundance, *i.e.* equimolar or 1:1 mixtures of *rac* and *meso* diastereomers. This equality of abundance implies that the formation of these stereoisomers is statistically controlled, *i.e.* the chirality of the first Si atom attached to the nitrogen atom does not lead to a preferred chirality for the second Si. We note also that the *rac*:*meso* ratio for **2** did not depend on the solvent chosen for the synthesis, *n*-pentane or tetrahydrofuran (thf) (see Experimental and Theoretical Procedures).

**Table 3** Infrared bands ( $\text{cm}^{-1}$ ) observed for compounds **1** and **2**

<b>1</b>		<b>2</b>		Assignment
Gas	Liquid	Gas	Liquid	
This work	Ref. 5	This work	Ref. 5	
3397w	3360s			$\nu(\text{NH})$
2977mw	2970w	2975w	2970w	$\nu_{\text{asym}}[\text{CH}_3(\text{Si})]$
		2950w	2950w	$\nu_{\text{asym}}[\text{CH}_3(\text{N})]$
2918w		2914w	2900w	$\nu_{\text{sym}}[\text{CH}_3(\text{Si},\text{N})]$
2851w		2851w		$2 \times \delta_{\text{asym}}[\text{CH}_3(\text{Si})]$
		2834w	2820w	$2 \times \delta_{\text{sym}}[\text{CH}_3(\text{N})]?$
2218w(sh)		2218(sh)		$\text{SiHMeCl}_2$
2192.4s	2200s	2208.1m	2200s	$\nu(\text{SiH})$
		2180.5m		$\nu(\text{SiH})$
<i>a</i>	1410m	<i>a</i>	1410vw	$\delta_{\text{asym}}[\text{CH}_3(\text{Si})]$ , $\delta_{\text{asym}}[\text{CH}_3(\text{N})]$
1266ms	1260s	1266m	1260s	$\delta_{\text{sym}}[\text{CH}_3(\text{Si})]$
		1202mw	1200m	$\rho[\text{CH}_3(\text{N})]$
1188s	1190s			$\delta[\text{NH}(\text{N})]$
1102w(br)				?
		1090m	1090m	$\nu(\text{CN})$
		1079m	1070m	$\nu(\text{CN})$
950vs	950s	946vs	950vs	$\nu_{\text{asym}}(\text{NSi}_2)$
881s(sh)		885s		$\delta(\text{SiH})$
858vs	840vs	852s	850vs	$\delta(\text{SiH})$
805m <sup>b</sup>				$\rho(\text{CH}_3)$
754ms	750s	760m	750m	$\rho(\text{CH}_3)$
633w <sup>b</sup>				?
566w				?
517s	500vs	511s	500s	$\nu(\text{SiCl})$

<sup>a</sup> Region obscured by uncompensated atmospheric water lines and window bands. <sup>b</sup> Corresponding features are seen in the liquid-phase spectra.

**Fig. 2** The  $\nu(\text{Si-H})$  bands from the IR spectrum of compounds **1** (dotted) and **2**

The  $^1\text{H}$  NMR spectrum of compound **3** also displays a significant splitting of the resonances. Again this has to arise from the presence of chemically similar but non-equivalent species. However, in this case the resonances are of unequal intensity, which requires closer scrutiny. There are four possible stereoisomers for **3**: *1R,5R-3*, *1S,5S-3*, *1R,5S-3* and *1S,5R-3*. The former two form a pair of enantiomers, thus **3** may consist of three chemically different diastereomers. The last two diastereomers are not identical, due to the presence of the pseudo-asymmetrical atom Si<sup>3</sup>. The two NMe(SiHMeCl) groups of *1R,5R-3* are diastereotopic to each other and should give rise to two sets of signals. Each of these groups is enantiotopic to one in *1S,5S-3*, so that a racemic mixture of both should result in two sets of signals having equal intensities. For *1R,5S-3*, however, the two NMe(SiHMeCl) groups are enantiotopic to each other but diastereotopic to those of *1S,5R-3* and to both sets of *1R,5R-3* and *1S,5S-3*. As *1R,5S-3* and *1S,5R-3* are diastereomers, with differing sets of signals, the latter need not have equal intensities. Since the  $^1\text{H}$  NMR spectrum of **3**

showed *just* two sets of non-equal intensities, we conclude that **3** consists of a non-equimolar mixture of the *1R,5S* and *1S,5R* diastereomers *only*, which are the ones shown in Scheme 1.

### Infrared spectra

Table 3 lists the frequencies observed in the gas phase in this work, and in the liquid from the earlier study.<sup>5</sup> Bearing in mind that only the stronger bands seen in the latter's spectra were reported, the agreement between the gas- and liquid-phase spectra is good. Inspection of the liquid-phase spectra provided by the authors showed several differences of detail. A downwards shift of  $37\text{ cm}^{-1}$  in  $\nu(\text{NH})$  from the gas to the liquid together with a marked increase in relative intensity indicate a degree of hydrogen bonding in the latter phase which corroborates the evidence from the NMR results in solution (see above). A similar shift of  $33\text{ cm}^{-1}$  was found in the case of  $\text{NH}(\text{SiHCl}_2)_2$ .<sup>9</sup> The doublet with  $38\text{ cm}^{-1}$  spacing observed in the gas-phase  $\nu(\text{SiH})$  region of compound **2** is replaced in the liquid by a single broad, slightly asymmetric band with a half-width of about  $55\text{ cm}^{-1}$ . (The corresponding band for **1** in the liquid is also broad, but a peak absorption of about 100% prevented a measurement of half-width.) In addition our spectrum of **1** contained a small amount of  $\text{SiHMeCl}_2$ , identified from the appearance in varying amounts of the tip of the very intense, narrow Q branch at  $2218\text{ cm}^{-1}$  of its  $\nu(\text{SiH})$  band, as seen in Fig. 2. A minute trace of this impurity occurred also in **2**, where a very weak shoulder at  $2218\text{ cm}^{-1}$  can just be discerned (Fig. 2). The presence of  $\text{SiHMeCl}_2$  is attributed to thermolysis in the cell, rather than to hydrolysis, since no HCl was visible in the spectrum. The contour of the  $2218\text{ cm}^{-1}$  band limits interference to the immediate neighbourhood of its peak, leaving the bands due to **1** and **2** unaffected.

The assignments given in Table 3 are based on the unscaled frequencies from the Gaussian SCF/6-31G\* calculations.<sup>4</sup> Of the modes which vary little with conformation, the *ab initio* results indicate that there is little difference in the  $\nu(\text{CH})$  values for the NMe and SiMe groups, but large ones in the  $\delta_{\text{asym}}(\text{CH}_3)$  and  $\delta_{\text{sym}}(\text{CH}_3)$  modes, the latter markedly larger when the methyl group is attached to the nitrogen atom. This is as expected. The presence of overtones of both  $\delta_{\text{asym}}(\text{CH}_3)$  and  $\delta_{\text{sym}}(\text{CH}_3)$  in the middle of the  $\nu(\text{CH}_3)$  region for the NMe group therefore makes assessment of the very strong Fermi resonances present here difficult.

Modes which are found to vary significantly with conformation include  $\nu(\text{NH})$ ,  $\nu(\text{SiH})$ ,  $\delta(\text{NH})$ ,  $\delta(\text{SiH})$ ,  $\rho(\text{CH}_3)$ ,  $\nu_{\text{sym}}(\text{NSi}_2)$ ,  $\nu(\text{SiCl})$  and skeletal bends, all of which are potentially at least a source of information about the conformers present. A minor variation in  $\nu_{\text{asym}}(\text{NSi}_2)$  due to coupling with the highest  $\delta(\text{SiH})$  motion is likely to be an illusion arising from the absence of the differing scale factors that will be needed if the observed frequencies involving these two types of motion are to be fitted exactly. In fact, a proper analysis of all except one of these variations must await the calculation of scaled *ab initio* force fields, for which purpose it will be necessary to transfer scale factors from the parent molecules  $\text{NH}(\text{SiH}_3)_2$  and  $\text{NMe}(\text{SiH}_3)_2$ , currently under study. However information from the  $\nu(\text{SiH})$  region needs no such assistance and we may proceed directly to see what this reveals.

**Analysis of the  $\nu(\text{SiH})$  region.** It is helpful if we place the data for the current compounds **1** and **2** in the context of previous work on disilylamines. Table 4 includes all such  $\nu(\text{SiH})$  data so far available, while Fig. 2 shows the expanded  $\nu(\text{SiH})$  regions of **1** and **2**. Our eventual objective is to explain why all the disilylamines bearing an N-H group show a single, broad, often asymmetric band whereas all the disilylamines with an N-Me group exhibit two peaks.

The starting point for our analysis of these spectra are the predictions from the *ab initio* calculations<sup>4</sup> that for both com-

pounds six conformers are present at room temperature, as shown in Table 5. For each conformer we give the two dihedral angles  $\tau(\text{HSi}^i\text{NX})$  ( $X = \text{H}$  for **1** and **C** for **2**), the Si–H bond lengths  $r(\text{Si–H})$ , the  $\nu(\text{SiH})$  frequencies  $\nu_1$  and  $\nu_2$  for the  $\text{D}_0$  (not deuteriated) and  $\text{D}_1$  (one Si–D bond) species (the latter being the  $\nu_{\text{is}}$  values), the calculated infrared intensities for the  $\text{D}_0$  species bands [before ( $A$ ) and after ( $Ax$ ) weighting with the abundance,  $x$ , calculated at the MP2/6-311+G\* level for each conformer] and finally the interaction force constant  $f'$ . (Dipole derivatives with respect to bond stretching and related quantities will be given in a later paper.<sup>15</sup>) The usual good correlation

between  $\nu_{\text{is}}(\text{SiH})$  and  $r(\text{Si–H})$  obeys equation (1) with an  $R$  factor of 0.9959.

$$\nu_{\text{is}}(\text{SiH})/\text{cm}^{-1} = 13\,103(227) - 72.8(16) r(\text{Si–H})/\text{pm} \quad (1)$$

Some striking results emerge. Quite large splittings of the two  $\nu(\text{SiH})$  frequencies occur in nearly all the conformers up to a maximum of  $38.5\text{ cm}^{-1}$ . Those in compound **1**, however, tend to be about one-half of those in **2**. The splittings arise from two sources. The largest occur where the  $\text{D}_0$  and  $\text{D}_1$  frequencies are identical, indicating zero coupling between the two Si–H stretching motions, with a zero value of the interaction constant  $f'$ . In each case the two Si–H bonds concerned have very different orientations with respect to the skeletal plane, as indicated by the torsion angles involved, *e.g.*  $176.2$  and  $-48.1^\circ$  for *rac*-**2A** [see Table 5(b)]. Similarly, their bond lengths are different.

However, splittings as large as  $19.8\text{ cm}^{-1}$  occur in situations such as in *meso*-**2B**, where the Si–H bonds are identical with respect to their orientations, lengths and force constants. The coupling constant responsible,  $f'$ , can be as large as  $2.42\text{ N m}^{-1}$  (*rac*-**2B**). This constant, linking as it does bonds which are *gamma* related, is of comparable size with the similar constant between bonds which are *alpha* related, in  $\text{SiH}_3$  or  $\text{SiH}_2$  groups,<sup>16</sup> but is much larger than those for *beta*-related bonds, either *trans* or *gauche*, measured in disilanes.<sup>16–20</sup>

The corresponding  $f'$  in  $\text{CH–X–CH}$  systems is quite negligible, as may be seen by the close similarity of the  $\nu(\text{CH})$

**Table 4** Infrared bands ( $\text{cm}^{-1}$ ) in the  $\nu(\text{SiH})$  regions of disilylamines in the gas phase

Molecule	Bands	Average	Ref.
$\text{NH}(\text{SiH}_3)_2$	2164.4 (br)as	2164.4	13
$\text{NMe}(\text{SiHD}_2)_2$	2144.5, <i>ca.</i> 2184	2164.3	8
$\text{NMe}(\text{SiH}_2\text{Me})_2$	2128.0, 2165.3	2146.7	7
$\text{NH}(\text{SiHMe}_2)_2$	2128.3	2128.3	7
$\text{NMe}(\text{SiHMe}_2)_2$	2113.4, 2153.2	2133.3	7
$\text{NH}(\text{SiHCl}_2)_2$	2247 (br)	2247	9
$\text{NMe}(\text{SiHCl}_2)_2$	2232.5, 2237 (sh), <sup>a</sup> 2253.4, 2260 (sh) <sup>b</sup>	2243.0	14
$\text{NH}(\text{SiHMeCl})_2$	2192.4 (br)as, 2218sp (sh) <sup>c</sup>	2192.4	This work
$\text{NMe}(\text{SiHMeCl})_2$	2180.5, 2208, 2218 (sh) <sup>d</sup>	2194.3	This work

<sup>a</sup> Possibly due to  $\text{SiH}_2\text{Cl}_2$ . <sup>b</sup> Possibly due to  $\text{SiHCl}_3$ . <sup>c</sup> Variable intensity and due to  $\text{SiHMeCl}_2$  impurity. <sup>d</sup> Probably due to  $\text{SiHMeCl}_2$  impurity.

**Table 5** The SCF/6-31G\* data for Si–H bonds

	Conformer					
	<i>rac</i>			<i>meso</i>		
	A	B	C	A	B	C
(a) Compound <b>1</b>						
$\tau_1(\text{HSi}^1\text{NH})^\circ$	150.5	161.7	−17.9	155.2	167.8	−10.6
$\tau_2(\text{HSi}^2\text{NH})^\circ$	−52.8	161.7	−17.9	27.7	−167.8	51.7
$r_1(\text{Si–H})/\text{pm}$	146.51	146.43	146.68	146.48	146.46	146.72
$r_2(\text{Si–H})/\text{pm}$	146.77	146.43	146.68	146.69	146.46	146.76
$\nu_1(\text{D}_0)/\text{cm}^{-1}$	2435.98	2448.34	2427.61	2439.85	2447.76	2423.92
$\nu_2(\text{D}_0)/\text{cm}^{-1}$	2417.11	2437.07	2423.95	2424.71	2433.91	2417.11
$(\nu_1 - \nu_2)/\text{cm}^{-1}$	18.9	11.3	3.7	15.1	13.9	6.8
$\nu_{\text{is},1}/\text{cm}^{-1}$	2435.92	2442.74	2425.77	2439.85	(2440.8) <sup>a</sup>	2423.34
$\nu_{\text{is},2}/\text{cm}^{-1}$	2417.15	2442.74	2425.77	2424.71	(2440.8) <sup>a</sup>	2417.69
$A_1/\text{km mol}^{-1}$	166.7	259.6	204.0	154.5	300.0	212.6
$A_2/\text{km mol}^{-1}$	209.4	40.5	198.9	199.5	2.9	201.4
$x^b$	0.102	0.165	0.233	0.348	0.081	0.072
$A_1x/\text{km mol}^{-1}$	17.0	42.8	47.5	53.8	24.3	15.3
$A_2x/\text{km mol}^{-1}$	21.4	6.7	46.3	69.4	0.2	14.5
$f'(\text{full})/\text{N m}^{-1}$	0.20	1.33	0.50	0.04	<sup>c</sup>	0.50
$f'(\text{HLM})/\text{N m}^{-1}$	0.35	1.58	0.51		1.94	0.53
(b) Compound <b>2</b>						
$\tau_1(\text{HSi}^1\text{NC})^\circ$	176.2	169.8	−30.5	166.2	174.8	−22.6
$\tau_2(\text{HSi}^2\text{NC})^\circ$	−48.1	173.1	−28.1	37.0	−175.0	54.2
$r_1(\text{Si–H})/\text{pm}$	146.31	146.35	146.63	146.34	146.38	146.63
$r_2(\text{Si–H})/\text{pm}$	146.82	146.36	146.70	146.71	146.38	146.83
$\nu_1(\text{D}_0)/\text{cm}^{-1}$	2451.88	2456.06	2426.76	2449.95	2454.61	2426.66
$\nu_2(\text{D}_0)/\text{cm}^{-1}$	2413.34	2436.96	2421.83	2421.17	2434.80	2412.35
$(\nu_1 - \nu_2)/\text{cm}^{-1}$	38.5	19.1	4.9	28.8	19.8	14.3
$\nu_{\text{is},1}/\text{cm}^{-1}$	2451.87	2447.11	2425.71	2449.93	(2444.7) <sup>a</sup>	2426.32
$\nu_{\text{is},2}/\text{cm}^{-1}$	2413.34	2446.09	2422.88	2421.17	(2444.7) <sup>a</sup>	2412.70
$A_1/\text{km mol}^{-1}$	160.5	279.5	135.6	160.0	295.3	184.9
$A_2/\text{km mol}^{-1}$	189.8	19.4	222.5	179.1	7.7	186.5
$x^b$	0.196	0.258	0.046	0.300	0.131	0.069
$A_1x/\text{km mol}^{-1}$	31.5	72.1	6.2	48.0	38.7	12.8
$A_2x/\text{km mol}^{-1}$	37.2	5.0	10.2	53.7	1.0	12.9
$f'(\text{full})/\text{N m}^{-1}$	0.04	2.42	0.56	<0.01	<sup>c</sup>	0.57
$f'(\text{HLM})/\text{N m}^{-1}$	0.00	2.67	0.56	<0.01	1.98	0.61

<sup>a</sup> Average of  $\nu_1$  and  $\nu_2$ . <sup>b</sup> The molar fractions  $x$  are those from MP2 calculations, Table 3 in ref. 4, for slightly different torsional angles. <sup>c</sup> Cartesian force constants not available.

region of the IR spectra of species such as  $\text{NMe}_3$  and  $\text{NMe}(\text{CD}_3)_2$  etc., or by examining scaled *ab initio* force fields.<sup>21,22</sup>

There are several clues as to the origin of this large value of  $f'$  in  $\text{SiH}-\text{Y}-\text{SiH}$  systems. (1) It is associated with  $\text{Si}-\text{H}$  bonds which are almost parallel, but is absent where the bonds are not so, for example in *rac*-**1C**, where the two bonds are identically disposed but point in very different directions. The widely differing infrared intensity distributions of  $\nu_1$  and  $\nu_2$  for the various conformers reflect these differences in the mutual orientation of the  $\text{Si}-\text{H}$  bonds. (2) In a similar calculation for the  $\text{C}_{2v}$  conformer of  $\text{NH}(\text{SiHCl}_2)_2$ ,<sup>15</sup> where both SCF and MP2 treatments were available, the value of  $f'$  diminishes as the infrared intensity diminishes, from the SCF to the MP2 calculation. These facts suggest a transition dipole–transition dipole mechanism for the interaction which reflects the much greater infrared intensity associated with the stretching of  $\text{Si}-\text{H}$  bonds as compared to  $\text{C}-\text{H}$  ones. This will be examined quantitatively in a later publication.<sup>15</sup>

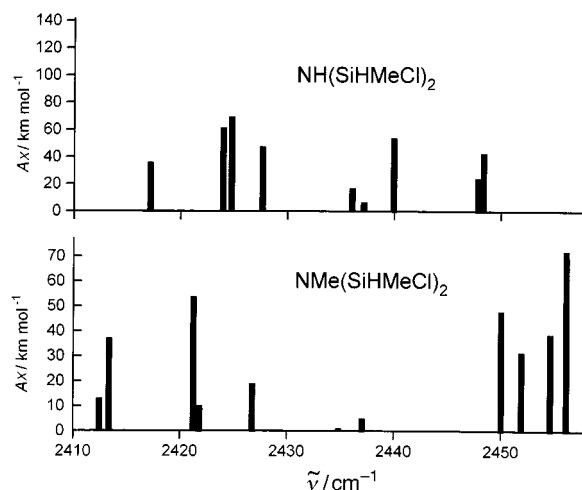
For our present purpose in trying to understand the difference between the IR spectra of compounds **1** and **2**, we now compare the predicted infrared spectra as column diagrams for the two compounds in Fig. 3. There is a very clear-cut separation of the absorption for compound **2** into two distinct regions separated by about  $33\text{ cm}^{-1}$ . By contrast, for **1**, while most of the absorption occurs near  $2425\text{ cm}^{-1}$ , a high proportion occurs near  $2440$  and  $2448\text{ cm}^{-1}$ , enough to make a doublet appearance possible, but one with a much smaller spacing than for the  $\text{NMe}$  compound. Any broadening effect could readily merge the whole into one broad band.

In comparing these with the observed spectra several factors must be borne in mind. First, the frequencies will be overestimated by the SCF/6-31G\* calculation by about 9%. Our experience suggests that the primary effect of this on force constants expressed in internal coordinates is on the diagonal constants, not the interaction ones.<sup>17–19</sup> Secondly, the *ab initio* approach may not reproduce quantitatively the effects of the torsion angle on the  $\text{Si}-\text{H}$  force constants. The effect of chlorine substitution, for instance, is overestimated at this level of treatment.<sup>17–19</sup> Thirdly, if the coupling between the stretching motions arises from a dipole–dipole mechanism, this will have been overestimated in so far as *ab initio* intensities generally exceed experimental ones for this type of motion by at least a factor of two.<sup>23</sup> In such a case, therefore, ‘observed’ coupling constants are likely to be smaller than those predicted here.¶ This last consideration leaves little doubt that the observed separation of about  $30\text{ cm}^{-1}$  in the two  $\nu(\text{SiH})$  peaks of **2** arises primarily from the conformational dependence of  $\nu_{\text{is}}(\text{SiH})$  in *rac*-**2A** and *meso*-**2A** which together constitute 50% of the sample, according to the MP2 estimates of abundance. If the above is the correct interpretation, then the infrared spectrum in the  $\nu(\text{SiH})$  region of the partially deuteriated isotopomer of compound **2**,  $\text{NMe}(\text{SiHMeCl})(\text{SiDMeCl})$ , should be very similar to that of the undeuteriated one, as is the case for the corresponding species of  $\text{NMe}(\text{SiH}_3)_2$ .<sup>13</sup>

The  $\nu(\text{SiH})$  region in the IR spectrum of compound **1** is harder to understand. The two highest component bands calculated to lie near  $2448\text{ cm}^{-1}$  are both intense and if the coupling that has produced them has been overestimated their absorption would be expected at lower energy, coinciding with the  $2440\text{ cm}^{-1}$  band. An overall doublet spacing of about  $15\text{ cm}^{-1}$  would then result. It is interesting that the *ab initio* calculations of frequency indicate that the *average* frequency is almost

**Table 6** The SCF/6-31G\* torsional frequencies ( $\text{cm}^{-1}$ ) for compounds **1** and **2**

Compound	Conformer					
	<i>rac</i>			<i>meso</i>		
	A	B	C	A	B	C
<b>1</b>	19.8	24.8	29.0	25.3	12.4	25.5
	38.8	27.9	38.5	32.2	39.3	38.6
<b>2</b>	16.6	21.0	21.2	23.4	20.1	17.9
	35.9	28.1	24.4	29.1	36.1	39.1



**Fig. 3** Infrared spectra in the  $\nu(\text{SiH})$  regions of compounds **1** and **2**, as predicted *ab initio*. Frequencies and intensities are from SCF/6-31G\* calculations; conformer abundances were determined at the MP2/6-311+G\* level

unchanged, that is the chemical effect of *N*-methyl substitution on the  $\text{Si}-\text{H}$  bond is negligible: average values are: **2**,  $2433.9$ ; **1**,  $2435.9\text{ cm}^{-1}$ ; when weighted by the MP2 abundances these become  $2437.4$  and  $2434.2\text{ cm}^{-1}$  respectively. A more reliable indication comes from calculations for the structures of  $\text{NH}(\text{SiHCl}_2)_2$  and  $\text{NMe}(\text{SiHCl}_2)_2$  where both  $\text{Si}-\text{H}$  bonds are exactly in the skeletal plane and roughly parallel to each other.<sup>3</sup> The difference in the average  $\nu_{\text{is}}(\text{SiH})$  is only  $1.7\text{ cm}^{-1}$ ,  $\text{NMe}(\text{SiHCl}_2)_2 > \text{NH}(\text{SiHCl}_2)_2$ .<sup>23</sup>

Since the frequency of the single band for  $\nu(\text{SiH})$  observed in the IR spectrum of compound **1** lies close to the average of the two seen in the spectrum of **2**, it is likely that it represents an average of frequencies which are continuously varying. The interconversion of conformers would then be taking place on a time-scale short compared with about  $2.2 \times 10^{-11}\text{ s}$ . This, however, raises the question as to why the same effect does not operate in **2**. Table 6 compares the two lowest vibration frequencies for the six conformers of **1** and **2**, which may be taken to be essentially torsional motions of the  $\text{SiHMeCl}$  groups against the  $\text{Si}-\text{N}-\text{Si}$  skeleton. The values are all real, in contrast to what is found for  $\text{NH}(\text{SiHCl}_2)_2$ ,<sup>3</sup> while the frequencies for **1** are slightly larger than those for **2** except in the case of the *meso*-**B** conformers. Taking into account also that many molecules will be in torsionally excited states well above the likely barrier to internal rotation of the  $\text{SiHMeCl}$  group, we conclude that the time-scales for interconversion are likely to be essentially the same in the two compounds. The  $\nu(\text{SiH})$  splittings must therefore be either just above or just below the critical value at which signal averaging takes place.

If free rotation is occurring on the infrared time-scale for compound **1**, it is natural to extend the explanation to the other disilylamines bearing an  $\text{NH}$  group (see Table 5), namely  $\text{NH}(\text{SiH}_3)_2$ ,  $\text{NH}(\text{SiHMe}_2)_2$  and  $\text{NH}(\text{SiHCl}_2)_2$ , as has been suggested for the first two of these.<sup>7</sup> However this involves the

¶ Calculations at both SCF and MP2 levels for  $\text{NH}(\text{SiH}_3)_2$  and  $\text{NMe}(\text{SiH}_3)_2$  show that the MP2-based interaction constants are slightly less than the SCF ones and indistinguishable from those observed experimentally. By contrast, variations in  $\nu_{\text{is}}(\text{SiH})$  and  $r(\text{Si}-\text{H})$  of the kind found in this work are slightly larger at the MP2 level, the former again in excellent agreement with experiment.<sup>13</sup>

**Table 7** The SCF/6-31G\* data for Si-Cl bonds in compounds **1** and **2**

	Conformer					
	<i>rac</i>			<i>meso</i>		
	A	B	C	A	B	C
<b>Compound 1</b>						
$\tau_3(\text{ClSi}^1\text{NH})/^\circ$	−93.8	−82.9	96.7	−89.5	−76.0	104.9
$\tau_4(\text{ClSi}^2\text{NH})/^\circ$	61.4	−82.9	96.7	−86.7	76.0	−62.4
$r_1(\text{Si}^1\text{—Cl})/\text{pm}$	208.22	208.52	208.58	208.55	208.06	208.14
$r_2(\text{Si}^2\text{—Cl})/\text{pm}$	208.06	208.52	208.58	208.56	208.06	208.05
$f(\text{Si}^1\text{—Cl})/\text{N m}^{-1}$	291.74	288.39	287.52	287.96	*	292.83
$f(\text{Si}^2\text{—Cl})/\text{N m}^{-1}$	294.11	288.39	287.52	287.93	*	294.20
$f'/\text{N m}^{-1}$	4.14	2.32	1.76	2.10	*	4.10
<b>Compound 2</b>						
$\tau_3(\text{ClSi}^1\text{NH})/^\circ$	−67.6	−74.4	83.5	−78.2	−68.8	92.3
$\tau_4(\text{ClSi}^2\text{NH})/^\circ$	65.6	−71.3	85.5	−76.8	68.6	−59.4
$r_1(\text{Si}^1\text{—Cl})/\text{pm}$	208.42	208.69	209.05	208.67	208.33	208.57
$r_2(\text{Si}^2\text{—Cl})/\text{pm}$	208.50	208.92	208.78	208.98	208.33	208.44
$f(\text{Si}^1\text{—Cl})/\text{N m}^{-1}$	289.37	286.18	281.81	286.41	*	287.47
$f(\text{Si}^2\text{—Cl})/\text{N m}^{-1}$	288.47	283.57	285.09	282.80	*	289.37
$f'/\text{N m}^{-1}$	4.19	2.61	2.16	2.42	*	4.16

\* Cartesian force constants not available.

difficulty that replacement of a methyl group by a chlorine atom raises  $\nu(\text{SiH})$  by  $64\text{ cm}^{-1}$ , on passing from  $\text{NH}(\text{SiHMe}_2)_2$  to  $\text{NH}(\text{SiHMeCl})_2$ , while the further replacement between  $\text{NH}(\text{SiHMeCl})_2$  and  $\text{NH}(\text{SiHCl}_2)_2$  causes an additional rise of  $55\text{ cm}^{-1}$ . These shifts are markedly larger than those from  $\text{SiH}_2\text{Me}_2$  to  $\text{SiH}_2\text{MeCl}$  ( $43.8\text{ cm}^{-1}$ ) and from  $\text{SiHMe}_2\text{Cl}$  to  $\text{SiHMeCl}_2$  ( $43.4\text{ cm}^{-1}$ ).<sup>7</sup> By contrast, the low frequency shift from  $\text{NH}(\text{SiH}_3)_2$  to  $\text{NH}(\text{SiHMe}_2)_2$  ( $36\text{ cm}^{-1}$ ) is normal for a pair of methyl groups.<sup>7</sup>

Two explanations of the enhanced shifts arising from chlorine substitution suggest themselves. (1) The internal rotation is not completely free but limited to a range of torsion angles favouring the preferred staggered arrangement of Me or Cl groups as seen along the  $\text{Si} \cdots \text{Si}$  axis, a common feature of the structure of compounds of this type.<sup>4</sup> However, without a more detailed study of the dependence of  $\nu(\text{SiH})$  on the torsion angle, it is not obvious how this will affect the distribution of  $\nu(\text{SiH})$  values to be averaged. This is an area we are currently exploring.<sup>13</sup> (2) There may be a chemical influence on the Si-H bond not only from  $\alpha$  substituents on the same silicon atom but also from those on the remote silicon. Evidence from SCF calculations on  $\text{NH}(\text{SiHCl}_2)_2$  and  $\text{NMe}(\text{SiHCl}_2)_2$  supports this latter view.<sup>15</sup>

A final question is: why are the splittings in the  $\nu(\text{SiH})$  frequencies in the conformers of compound **1** much smaller than those in **2**? The change in the dipole-dipole coupling prominent in the *rac*-**B** conformers can be wholly accounted for by the change in the H-Si-N-H(C) torsion angles from **1** to **2** and the resultant effects on the  $\text{H} \cdots \text{H}$  distance and mutual orientation of the two Si-H bonds. The dipole derivatives in the two compounds are found to be identical.<sup>15</sup> About half of the difference in the splittings in  $\nu_{\text{is}}(\text{SiH})$  can also be attributed to this cause. Thus a calculation of  $\nu_1$  and  $\nu_2$  for a non-equilibrium *rac*-**1** structure in which the H-Si-N-H angles are constrained to  $176.2$  and  $-48.1^\circ$  (values for *rac*-**2A**), yields the values  $2446.4$  and  $2418.9\text{ cm}^{-1}$ , a separation of  $27.5\text{ cm}^{-1}$ , somewhat larger than the  $18.9\text{ cm}^{-1}$  found for the equilibrium structure *rac*-**1A**, but still smaller than the  $38.5\text{ cm}^{-1}$  for *rac*-**2A**. Further exploration of these and related compounds will be needed to elucidate the sources of these small structural changes.

One important new conclusion regarding the interpretation of the infrared spectra of this type of compound can now be drawn. The theoretical prediction of long-range couplings between Si-H stretching motions means that it can no longer be assumed, as in earlier work,<sup>7</sup> that observation of several  $\nu(\text{SiH})$

stretching frequencies for a compound is *necessarily* an indication of the presence of non-equivalent Si-H bonds.

**Ab initio results for Si-Cl bonds.** While there are no group frequencies to be expected from Si-Cl stretching motions, such as occur for Si-H ones, we may use the *ab initio* force fields in internal coordinates to examine Si-Cl stretching force constants for signs of variation with respect to orientation in the molecule. The appropriate data are shown in Table 7. The excellent correlation between bond length and force constant obeys equation (2) with an *R* factor of  $-0.9994$ .

$$f(\text{Si-Cl})/\text{N m}^{-1} = 2831(23) - 112.19(11)R(\text{Si-Cl})/\text{pm}(2)$$

In most cases, the stronger Si-Cl bonds are associated with smaller values of  $|\tau_3|$  or  $|\tau_4|$ . There is a general tendency for the Si-Cl bonds to be slightly stronger in compound **1** than in **2**, but whether this arises from small differences in the torsion angles or from a direct chemical effect of methyl substitution at the nitrogen atom is not clear. Perhaps more surprising is the prevalence of sizeable stretch-stretch interaction constants, which are almost identical for corresponding conformers of **1** and **2**, despite differences in the torsion angles involved. (By contrast, there is no interaction between the two SiC stretches in any conformation.) The origin of these interactions would appear to be quite different from the dipole-dipole one for the  $\nu(\text{SiH})$  motions postulated above. A plausible source is the  $n(\text{N})-\sigma^*(\text{Si-Cl})$  interaction which is thought to influence the orientations found in the stable conformers.<sup>4</sup> If such is the case, the coupling term  $f'$  arises from an effect transmitted through a delocalised orbital centred on the nitrogen atom, rather than being a 'through-space' interaction as exemplified by the  $\nu(\text{SiH})-\nu(\text{SiH})$  coupling.

### Thermolysis

Kept at  $80^\circ\text{C}$  for 24 h, compounds **1** and **2** show a rather different behaviour: **1** decomposes to  $\text{NH}_4\text{Cl}$ ,  $\text{HSiMeCl}_2$  and oligosilazanes as could be shown by  $^1\text{H}$  NMR and mass spectrometry, whereas **2** stayed nearly unchanged and only small amounts of oligosilazanes could be detected by mass spectrometry.

### Reaction with pyridine

The reaction of compounds **1** and **2** with pyridine should reveal

the Brønsted acidity of **1** and the Lewis acidity of both compounds. This type of reaction has been used to study the Lewis and Brønsted acidities of  $\text{NH}(\text{SiCl}_3)_2$ <sup>24</sup> and  $\text{NH}(\text{SiHCl}_2)_2$ .<sup>9</sup>

No change of temperature was observed, either for compound **1** or **2**, when pyridine was added to a solution of the disilylamine in chloroform. Any reaction has thus to be slow and/or only slightly exothermic. In the case of **1**, all its characteristic peaks in the  $^1\text{H}$  NMR spectrum disappeared, the only clearly identifiable product being  $\text{SiHMeCl}_2$ . Peaks in the  $\text{H}(\text{Si})$  chemical shift range suggested that a variety of compounds containing  $\text{SiHMeCl}$  groups were formed. A very broad signal at  $\delta$  17.8 indicated the formation of either an  $\text{N}\cdots\text{H}\cdots\text{N}$  bridge or else of  $\text{NH}_4^+$ . As the peaks due to pyridine resembled strongly those of neat pyridine in  $\text{CHCl}_3$  the presence of  $\text{NH}_4\text{Cl}$  was inferred. Furthermore, we conclude that neither **1** nor any of its decomposition products forms a complex with pyridine, the latter acting as a decomposition catalyst towards **1**. In contrast, the  $^1\text{H}$  NMR spectrum of a mixture of **2** and pyridine was essentially the sum of the spectra of the pure compounds, indicating the absence of any reaction.

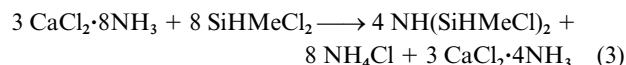
## Experimental and Theoretical Procedures

### Materials and instrumentation

All manipulations were performed either in a dry-box under an atmosphere of argon or nitrogen (dried with activated 4 Å molecular sieves and Sicapent®) or using a vacuum line. Solvents were distilled from  $\text{CaH}_2$  and stored over activated molecular sieves; gaseous  $\text{NH}_3$  and  $\text{NH}_2\text{Me}$  were dried by passing the vapours over 3 Å molecular sieves;  $\text{SiHMeCl}_2$  (Aldrich, 97%) was used without further purification and  $\text{CaCl}_2\cdot 8\text{NH}_3$  was prepared according to the method of Hüttig.<sup>25</sup> Elemental analyses (C, H, N) were performed with a LECO-1000 combustion analyser; Cl was determined potentiometrically with  $\text{AgNO}_3$ . Differential thermal analysis was performed using a Mettler TA 3000 instrument. Dipole moments of the liquids were measured using a WTW Dipolemeter DM 01. Gas-phase IR spectra were recorded in the range 4000–400  $\text{cm}^{-1}$  on a Perkin-Elmer Paragon 1000 spectrometer using a 10 cm gas cell at a resolution of 1  $\text{cm}^{-1}$ , filled with about 5 Torr (saturated) vapour pressure. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra were recorded on Bruker AMX 200 and AMX 400 instruments.

### Preparations

As both compounds **1** and **2** were reported to be thermally unstable even at ambient temperature,<sup>5</sup> we opted for a low-temperature synthesis which avoided the several hours of reflux at 55 °C associated with the previous method.<sup>5</sup> Our method also replaces the previously used starting materials of  $\text{NH}(\text{SiMe}_3)_2$  and  $\text{NMe}(\text{SiMe}_3)_2$  with the cheaper  $\text{CaCl}_2\cdot 8\text{NH}_3$  and  $\text{NH}_2\text{Me}$ . (An unexpected bonus was the isolation of compound **3** from the preparation of **2**.) Compound **1** was therefore synthesized according to equation (3), a variant of which has recently been

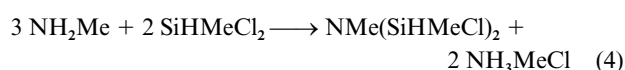


used to prepare  $\text{NH}(\text{SiHCl}_2)_2$ .<sup>9</sup> It was established earlier that only four of the eight  $\text{NH}_3$  molecules in  $\text{CaCl}_2\cdot 8\text{NH}_3$  are reactive towards  $\text{SiHCl}_3$  and elemental analysis of the solid residue confirmed that the same was true for the reaction with  $\text{SiHMeCl}_2$ .

The compound  $\text{CaCl}_2\cdot 8\text{NH}_3$  (8.95 g, 41.4 mmol, 290 mmol

$\text{NH}_3$ ) was added over a period of 4 h to a stirred solution of  $\text{SiHMeCl}_2$  (40  $\text{cm}^3$ , 386 mmol) in *n*-pentane (100  $\text{cm}^3$ ) maintained at –45 °C. The resulting suspension was subsequently stirred for 40 h at room temperature. The compounds  $\text{CaCl}_2\cdot 4\text{NH}_3$  and  $\text{NH}_4\text{Cl}$  were filtered off and washed twice with *n*-pentane (20  $\text{cm}^3$ ). After removing unchanged  $\text{SiHMeCl}_2$  and *n*-pentane *in vacuo* at –45 °C, the residue was warmed to 0 °C and fractionally distilled. The compound  $\text{NH}(\text{SiHMeCl})_2$  was condensed as a colourless liquid at –45 °C (7.0 g, 83%). On cooling to –196 °C it initially forms a glass which subsequently changes audibly into polycrystalline material. Differential thermal analysis did not reveal any melting process between –150 °C and room temperature, but instead showed conversion of a crystalline phase into a glass at –130 °C (Found: C, 12.7; H, 4.4; Cl, 39.6; N, 5.8; Si, 29.3. Calc. for  $\text{C}_2\text{H}_6\text{Cl}_2\text{NSi}_2$ : C, 13.8; H, 5.2; Cl, 40.7; N, 8.0; Si, 32.3%). \*\* EI mass spectrum:  $m/z$  173 (95, *M*), 158 (100, *M* – Me), 143 (5, *M* – 2Me), 138 (50, *M* – Cl), 123 (9, *M* – Cl – Me), 102 (8, *M* – Cl – 2Me) and 79 (28%,  $\text{SiHMeCl}$ ).  $\mu$  (0.001–0.01 mol  $\text{dm}^{-3}$  solutions in *n*-hexane) 2.27(6)†† D.  $d^{20}$  1.10  $\text{g cm}^{-3}$ .

Compound **2** was prepared according to equation (4).



Methylamine (30  $\text{cm}^3$ , 0.70 mol) was condensed over a period of 8 h into a stirred solution of  $\text{SiHMeCl}_2$  (365 g, 3.17 mol) in *n*-pentane (250  $\text{cm}^3$ ) maintained at –30 °C, and the mixture was stirred for 12 h at room temperature. The compound  $\text{NH}_3\text{MeCl}$  was filtered off and washed twice with *n*-pentane (50  $\text{cm}^3$ );  $\text{SiHMeCl}_2$  and *n*-pentane were distilled from the combined liquid phases at normal pressure and the residue was fractionally distilled *in vacuo*. Compound **2** was obtained as the main product (40 °C, 8 Torr; 17.0 g, 39%). Alternatively, a 2.0 mol  $\text{dm}^{-3}$  solution of  $\text{NH}_2\text{Me}$  in thf (50  $\text{cm}^3$ , 0.10 mol) was added dropwise over a period of 3 h to a stirred solution of  $\text{SiHMeCl}_2$  (25  $\text{cm}^3$ , 0.24 mol) in thf maintained at –30 °C and the mixture stirred for 12 h. The compound  $\text{NH}_3\text{MeCl}$  was filtered off and washed twice with thf (50  $\text{cm}^3$ );  $\text{SiHMeCl}_2$  and thf were removed *in vacuo* (0 °C) and the residue, kept at room temperature, fractionally distilled *in vacuo*. Compound **2** condensed as a colourless liquid at –30 °C (2.67 g, 43%). On cooling to –150 °C a glass is formed which changed to a polycrystalline material at –105 °C which in turn melted sharply at –56 °C (Found: C, 17.8; H, 5.29; Cl, 36.4; N, 6.1; Si, 29.4. Calc. for  $\text{C}_3\text{H}_{11}\text{Cl}_2\text{NSi}_2$ : C, 19.1; H, 5.90; Cl, 37.7; N, 7.4; Si, 29.8%). \*\* EI mass spectrum:  $m/z$  187 (89, *M*), 172 (100, *M* – Me), 157 (13, *M* – 2Me), 152 (61, *M* – Cl), 142 (17, *M* – 3Me), 137 (13, *M* – Cl – Me), 122 (31, *M* – Cl – 2Me), 117 (10, *M* – 2Cl), 108 (68, *M* – Cl – 3Me) and 79 (65%,  $\text{SiHMeCl}$ ).  $\mu$  (0.001–0.01 mol  $\text{dm}^{-3}$  solutions in *n*-hexane) 2.59(6)†† D.  $d^{20}$  1.13  $\text{g cm}^{-3}$ .

Compound **3** was isolated as a side product in the synthesis of **2** by the first route above. The product was obtained at 65 °C, 0.1 Torr (3.9 g, 15%). EI mass spectrum:  $m/z$  260 (4.5, *M*) and 225 (100%, *M* – Cl).

All three compounds are very sensitive towards moisture, a characteristic feature of those with a Si–Cl moiety. The thermal decomposition of **1** and **2** was tested as follows: small amounts of **1** and **2** were condensed into Pyrex tubes and sealed before heating to 80 °C for 24 h. The tubes were opened under an inert atmosphere and samples submitted for mass and NMR spectral examination. Compound **1**: EI mass spectrum:  $m/z$  411 {66,  $[\text{NSiHMe}(\text{SiHMeCl})-\text{}]_3$ }, 274 {35,  $[\text{NSiHMe}(\text{SiHMeCl})-\text{}]_2$ }, 173 (81, **1**) and 114 (38%,  $\text{SiHMeCl}_2$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C,

|| A further advantage of our approach is that the excess of  $\text{SiHMeCl}_2$  in the reaction products from the preparation of compound **2** may be readily recovered and used for a further reaction. When  $\text{NMe}(\text{SiMe}_3)_2$  is the starting material the reaction yields an inseparable mixture of  $\text{SiHMeCl}_2$  and  $\text{SiMe}_3\text{Cl}$ .

\*\* The less than perfect agreement between experimental and calculated values reflects the extreme moisture sensitivity of the compounds and the concomitant difficulties in manipulating them.

†† Value in parentheses denotes the estimated standard deviation.

SiMe<sub>2</sub>)  $\delta$  5.58 [q,  $^3J(\text{H-H})$  2.2,  $\text{HSiMeCl}_2$ ], 5.13 [q,  $^3J(\text{H-H})$  2.4,  $\text{NH}(\text{SiHMeCl})_2$ ], 4.99 [m,  $\text{H}(\text{Si})$ , oligomer], 1.89 [br s,  $\text{NH}(\text{SiHMeCl})_2$ ], 0.87 [d,  $^3J(\text{H-H})$  2.2,  $\text{HSiMeCl}_2$ ], 0.60 [d,  $^3J(\text{H-H})$  2.4 Hz,  $\text{NH}(\text{SiHMeCl})_2$ ] and 0.45 [m,  $\text{Me}(\text{Si})$ , oligomer]. Compound **2**: EI mass spectrum:  $m/z$  333 (44, tetrasilazane), 260 (50, **3**), 219 [56,  $(-\text{SiHMeNMe}-)_3$ ], 187 (59, **2**), 146 [89,  $(-\text{SiHMeNMe}-)_2$ ] and 114 (24%,  $\text{SiHMeCl}_2$ ); in the  $^1\text{H}$  NMR spectrum, no peaks other than those of **2** were observed.

For the reaction with pyridine the disilylamine (ca. 5 mmol) was dissolved in chloroform (25 cm<sup>3</sup>). The solution was stirred at room temperature while pyridine (2.0 cm<sup>3</sup>, 24.8 mmol) was added in portions of 0.2 cm<sup>3</sup> and the temperature was monitored during each addition. For an NMR study of the reaction, a few drops of the disilylamine were dissolved in  $\text{CDCl}_3$  (1.0 cm<sup>3</sup>), pyridine (0.1 cm<sup>3</sup>) was added and the sample tube sealed off.

### Force-field calculations

For each of the conformers calculated to be present<sup>4</sup> the *ab initio* Cartesian force field and atomic Cartesian coordinates output by the GAUSSIAN program<sup>26</sup> were input into the program ASYM 40 (an update of ASYM 20<sup>27</sup>) for transformation into an internal coordinate system, with output of valence force constants and frequencies for partially deuteriated isotopomers. The potential energy associated with the stretching of the two Si-H or Si-Cl bonds in each molecule is given by equation (5)

$$2V = f_1 r_1^2 + f_2 r_2^2 + 2f' r_1 r_2 \quad (5)$$

where  $r_1$  and  $r_2$  are the displacements in each bond,  $f_1$  and  $f_2$  the valence force constants and  $f'$  the stretch-stretch interaction.

The program ASYM 40 yielded directly the diagonal ( $f_1, f_2$ ) and the off-diagonal ( $f'$ ) constants, but for the Si-H bonds they may also be obtained very simply through a harmonic local mode (HLM) calculation from the *ab initio*-derived  $\nu(\text{SiH})$  frequencies of the  $\text{D}_0$  and  $\text{D}_1$  species.<sup>16,17</sup> In this type of calculation, sometimes called an energy-factored force field, all motions other than Si-H stretching are ignored. In general the HLM value of  $f'$  is closely similar to the value from the full normal coordinate treatment embodied in the *ab initio* calculation, reflecting the very small amount of motions other than Si-H stretching in the  $\nu(\text{SiH})$  normal coordinates. The Si-Cl bonds cannot of course be similarly treated, due to the extent to which observed ' $\nu(\text{SiCl})$ ' frequencies are associated with modes in which there is coupling to other motions in the molecule.

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### References

- G. Gundersen and D. W. H. Rankin, *Acta Chem. Scand., Ser. A*, 1984, **38**, 647.
- G. Gundersen, D. W. H. Rankin and H. E. Robertson, *J. Chem. Soc., Dalton Trans.*, 1985, 191.
- H. Fleischer, D. Hnyk, D. W. H. Rankin, H. E. Robertson, M. Bühl and W. Thiel, *Chem. Ber.*, 1995, **128**, 807.
- H. Fleischer, P. T. Brain, D. W. H. Rankin, H. E. Robertson, M. Bühl and W. Thiel, following paper and refs. therein.
- E. Bacqué, J.-P. Pillot, M. Birot, J. Dunoguès, G. Bourgeois and M. Pétraud, *J. Organomet. Chem.*, 1994, **481**, 167.
- D. C. McKean, *J. Mol. Struct.*, 1984, **113**, 251.
- D. C. McKean and I. Torto, *Spectrochim. Acta, Part A*, 1993, **49**, 1095.
- D. C. McKean, I. Torto, J. E. Boggs and K. Fan, *J. Mol. Struct.*, 1992, **260**, 27.
- H. Fleischer, K. Hensen, D. Burgdorf, R. Flindt, U. Wannagat, H. Bürger and G. Pawelke, *Z. Anorg. Allg. Chem.*, 1995, **621**, 239.
- H. J. Campbell-Ferguson, E. A. V. Ebsworth, A. G. MacDiarmid and T. Yoshioka, *J. Phys. Chem.*, 1967, **71**, 723.
- E. Hengge and F. Höfler, *Z. Naturforsch., Teil A*, 1971, **26**, 768.
- D. E. Webster, *J. Chem. Soc.*, 1960, 5132.
- H. Fleischer, D. C. McKean and I. Torto, unpublished work.
- H. Fleischer, K. Hensen and D. C. McKean, unpublished work.
- H. Fleischer, D. C. McKean, M. Bühl and W. Thiel, unpublished work.
- D. C. McKean, *Spectrochim. Acta, Part A*, 1992, **48**, 1335.
- D. C. McKean, M. H. Palmer and M. F. Guest, *J. Mol. Struct.*, 1996, **376**, 289.
- D. C. McKean, A. L. McPhail, H. G. M. Edwards, I. R. Lewis, V. S. Mastryukov and J. E. Boggs, *Spectrochim. Acta, Part A*, 1993, **49**, 1079.
- D. C. McKean, A. L. McPhail, H. G. M. Edwards, I. R. Lewis, W. F. Murphy, V. S. Mastryukov and J. E. Boggs, *Spectrochim. Acta, Part A*, 1995, **51**, 215.
- D. C. McKean, H. G. M. Edwards, I. R. Lewis, W. F. Murphy, V. S. Mastryukov and J. E. Boggs, *Spectrochim. Acta, Part A*, 1995, **51**, 2237.
- W. F. Murphy, F. Zerbetto, J. L. Duncan and D. C. McKean, *J. Phys. Chem.*, 1993, **97**, 581.
- D. C. McKean, G. P. McQuillan, W. F. Murphy and F. Zerbetto, *J. Phys. Chem.*, 1990, **94**, 4820.
- A. M. Coats, D. C. McKean and D. Steele, *J. Mol. Struct.*, 1994, **320**, 269.
- H. Moretto, P. Schmidt and U. Wannagat, *Z. Anorg. Allg. Chem.*, 1972, **394**, 125.
- G. F. Hüttig, *Z. Anorg. Allg. Chem.*, 1922, **123**, 31.
- GAUSSIAN 94, Revision C.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheesman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1995.
- L. Hedberg and I. M. Mills, *J. Mol. Spectrosc.*, 1993, **160**, 117.

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