DALTON
FULL PAPER

Gas-phase molecular structures of bis(chloromethylsilyl)amine and bis(chloromethylsilyl)methylamine by electron diffraction and *ab initio* calculations; experimental support for n(N)–σ*(Si–Cl) hyperconjugation ‡

Holger Fleischer,*,†,[a] **Paul T. Brain,**[a] **David W. H. Rankin,**[a] **Heather E. Robertson,**[a] **Michael Bühl**[b] **and Walter Thiel**[b]

[a] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
[b] *Institut für Organische Chemie der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland*

The gas-phase molecular structures of $NH(SiHMeCl)_2$ **1** and $NMe(SiHMeCl)_2$ **2** have been investigated by electron diffraction (ED) and by *ab initio* geometry optimisations at the MP2/6-31G* level. *Ab initio* calculations suggest six different conformers to be present for both compounds. They also predict that all conformers exhibit planar or nearly planar configurations at the N atom and that all the Si–Cl bonds are more or less orthogonal to the SiNSi plane, a feature that is supported by the ED refinement. Natural bond orbital analysis and an SCF deletion calculation showed an energy contribution of the n(N)–σ*(Si–Cl) hyperconjugative interaction of more than 80 kJ mol^{-1}, thus rationalising conformations that optimise an overlap of the two appropriate orbitals. The principal parameters (r_a) from electron diffraction for $NH(SiHMeCl)_2$ (with estimated standard deviations given in parentheses and *ab initio*-calculated values for the lowest-energy conformer given in square brackets) are: *r*(Si–N) 171.2(2) [173.7], *r*(Si–Cl) 206.2(1) [207.7], *r*(Si–C) 184.5(3) [186.4] pm; Si–N–Si 128.8(12) [131.3], N–Si–Cl 112.9(4) [111.3], N–Si–C 115.7(9) [112.0] and Cl–Si–C 102.6(6) [107.3]°. For $NMe(SiHMeCl)_2$: *r*(Si–N) 171.5(1) [173.7], *r*(Si–Cl) 207.1(1) [208.1], *r*(Si–C) 185.2(2) [186.8], *r*(N–C) 147.4(6) [148.1] pm; Si–N–Si 124.9(6) [123.7], N–Si–Cl 108.3(5) [110.4], N–Si–C 115.1(8) [112.4] and Cl–Si–C 107.3(7) [106.7]°.

As part of our systematic investigations of the gas-phase molecular structures of simple silicon compounds by electron diffraction (ED), disilylamines have been of interest to us for a long time.[1–6] The main aim of our studies was to investigate the influence of different groups bound to the Si atoms on the principal structural parameters of disilylamines, with special concern for the torsion angles around the N–Si bonds. The ED structures of Si-methylated disilylamines bearing an N–H group suggested that it is 1,3-repulsive forces between the groups bound to the Si atoms that determine the conformation,[5] *i.e.* the substituents appear to be staggered when viewed along Si···Si. Concerning the ED structure of $NH(SiHCl_2)_2$, this suggestion was supported by ED data, but not by an *ab initio* geometry opimisation at the MP2/6-31G* level, which favoured a structure which was eclipsed when viewed along Si···Si.[6] We therefore decided to investigate the gas-phase structures of $NH(SiHMeCl)_2$ **1** and $NMe(SiHMeCl)_2$ **2** by ED as well as by *ab initio* calculations to get a more detailed picture of the structural impact of Me/Cl exchange on the Si atoms in dislylamines. As was shown in the preceding paper[7] which describes the preparation, reactions and spectroscopic (IR, NMR) properties of these compounds, both consist of inseparable 1 : 1 mixtures of their *rac* and *meso* diastereomeric forms. Furthermore, under the experimental conditions each diastereomeric form is likely to be present as a mixture of several conformers in the gas phase. Thus, this investigation is seen as another challenge for the combined analysis of ED and *ab initio* data by the recently developed SARACEN method, allowing more complicated structures to be tackled with confidence by gas-phase electron diffraction.[8]

Experimental

Compounds **1** and **2** were prepared and purified as recently reported.[7] Electron-diffraction scattering intensities were recorded on Kodak Electron Image plates, using the Edinburgh diffraction apparatus[9,10] with nozzle-to-plate distances of 95 and 258 mm and an accelerating voltage of 44.5 kV. For both compounds, the nozzle was maintained at 343 K and the sample held at 318 K during exposures. Three plates were exposed for each compound at each camera distance. Data were obtained in digital form using a computer-controlled Joyce-Loebl Microdensitometer 6, with automatic location of plate centres and the usual scanning program.[11] Electron wavelengths were determined from the scattering patterns of gaseous benzene, recorded on the same occasions as the sample data. Calculations were carried out using established data-reduction[11] and least-squares-refinement programs.[12] Weighting points used in setting up the off-diagonal weight matrices are given in Table 1, together with other relevant data. In all calculations standard complex scattering factors were used.[13]

Ab initio geometry optimisations were performed using standard Hartree-Fock (HF) and MP2 methods and a 6-31G* basis set[14] with the GAUSSIAN 94 program package[15] (five d functions were used). Initial optimisations were carried out in C_1 symmetry without any constraints. Many different starting conformations were tried, affording a total of six minima for both compounds **1** and **2**. Analytical frequencies were obtained at the HF/6-31G* level followed by reoptimisation at the electron-correlated MP2/6-31G* level. The MP2/6-31G* parameters are given in Table 2. For the optimised geometries and for the ED refined structures, single-point energy calculations and dipole moment calculations were carried out at the MP2/6-311 + G* level, the results of which, together with the relative abundances of the single conformers, are given in Table 3.

---

† *Present address*: Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität, Mainz, Johann Joachim Becher Weg 24, D-55099 Mainz, Germany.

‡ *Non-SI unit employed*: D ≈ 3.33 × 10^{-30} C m.

Table 1 Weighting functions, correlation parameters and scale factors

Compound	Height/mm	Δs/nm^{-1}	s_{min}/nm^{-1}	w_1/nm^{-1}	w_2/nm^{-1}	s_{max}/nm^{-1}	Correlation	Scale factor	λ/pm
1	95.06	40	120	140	304	356	−0.266	0.825(24)	5.576
	258.08	20	20	40	140	164	0.374	0.794(14)	5.574
2	95.06	40	120	140	304	356	0.194	0.800(18)	5.576
	258.08	20	20	40	140	164	0.073	0.739(9)	5.575

Results

Molecular models

Since both compounds **1** and **2** are present as 1 : 1 mixtures of their *meso* and *rac* diastereomers according to ^{1}H NMR spectroscopy,[7] and *ab initio* calculations suggest the likely presence of several conformers for each diastereomer (see Table 2),§ all six conformational minima on the *ab initio* potential energy surface (PES), three for *meso*-**1** and three for *rac*-**1**, were considered for the refinement of the ED structure of **1**, with their relative abundances fixed at the values given in Table 3. For the structural refinement of **2** the conformers *meso*-**2C** and *rac*-**2C**, which were of <5% abundance, were neglected and the populations of *meso*-**2A**, *meso*-**2B**, *rac*-**2A** and *rac*-**2B** adjusted to the values given in the last column of Table 3. The ED data were consistent with these distributions of conformers, although it is of course possible that other compositions would also provide a satisfactory fit to the data.

All corresponding bond lengths and angles except for the Si–N–Si angle were assumed to be equal. This procedure is justified because the *ab initio* calculated differences for these bond lengths and angles over all the major conformers are within the usual experimental uncertainties for these parameters. Larger differences occurred only for less abundant conformers, so the difference is negligible, because its contribution to the overall scattering is so small. In the case of the Si–N–Si angle two different approaches were chosen for compounds **1** and **2**, both based on the *ab initio* calculated values for this parameter. For **2**, the '**A**' conformers, which were given a common Si–N–Si angle, showed slightly bigger values than the '**B**' conformers, which also were given a common Si–N–Si angle. Accordingly, an arithmetic average, a_1, and half the difference, a_2 [see Table 2(*b*)] were chosen as independent parameters. In the case of **1**, common Si–N–Si angles were given to conformers denoted by the same letter, *i.e. meso*-**1A** and *rac*-**1A**, *etc.* Considering that the difference between conformers '**C**' and '**B**' was calculated to be about twice as big as the difference between '**A**' and '**B**', only two parameters, a_1 and a_2 [see Table 2(*a*)], were necessary to describe these angles: Si–N–Si ('**A**') $= a_1 - a_2$; Si–N–Si ('**B**') $= a_1$; Si–N–Si ('**C**') $= a_1 + 2a_2$. The difference parameter, a_2, was only refined for **2**.

The geometries of the molecules were described by the parameters listed in Table 2. In each case, the two halves of the molecule were taken to be identical. Planarity at nitrogen was assumed as suggested by *ab initio* geometry optimisation, with both Si–N–X angles (X = H for **1** and X = C for **2**) being equal, thus leaving only one independent angle at the nitrogen atom. The angles at the silicon atom were defined by *a*(N–Si–Cl), *a*(N–Si–H), *a*(N–Si–C), *a*(Cl–Si–C) and *a*(C–Si–H), the ones including a hydrogen atom only refining for **2**. The overall conformations adopted by the molecules were described in terms of dihedral angles (τ), *i.e.* τ(Cl–Si–N–H) for **1** and τ(Cl–Si–N–C) for **2**. In the case of the *meso* diastereomers the first of the two Cl–Si–N–X torsions (X = H for **1** and X = C for **2**) refers to the Si atom with an *S* configuration, whereas for the *rac* diastereomers the torsions refer to the enantiomers in which both Si atoms have an *S* configuration (for details about the stereochemistry of **1** and **2** see ref. 7). The two Cl–Si–N–X torsions for each conformer were constrained together, so that only one independent parameter remained to describe them. The relationships between the two torsions in one conformer were again derived from the *ab initio* results (see Table 2) and were set as follows: *meso*-**1A**, $\tau_1 = \tau_2$; *meso*-**1B**, $\tau_1 = -\tau_2$; *meso*-**1C**, $\tau_1 = -\tau_2 + 40°$; *rac*-**1A**, $\tau_1 = -\tau_2 - 33°$; *rac*-**1B**, $\tau_1 = \tau_2$; *rac*-**1C**, $\tau_1 = \tau_2$; *meso*-**2A**, $\tau_1 = \tau_2$; *meso*-**2B**, $\tau_1 = -\tau_2$; *rac*-**2A**, $\tau_1 = -\tau_2$; *rac*-**2B**, $\tau_1 = \tau_2$.

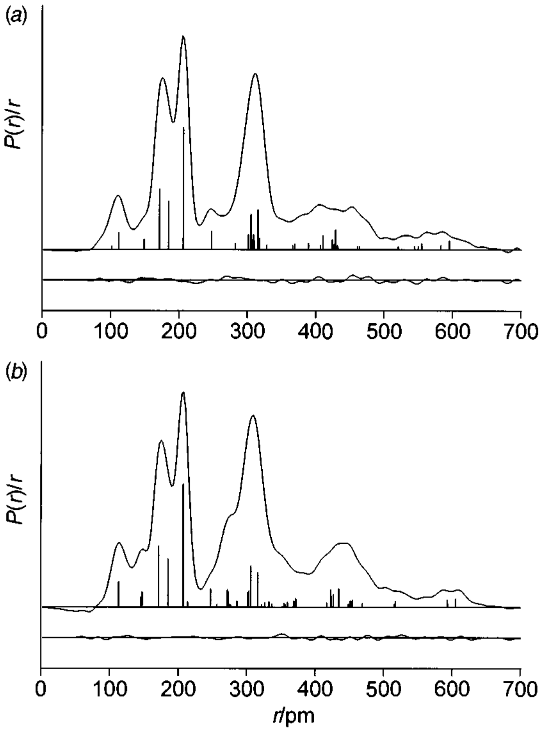

Fig. 1 Observed and final difference radial distribution curves, $P(r)/r$, for compounds **1** (*a*) and **2** (*b*). Before Fourier inversion the data were multiplied by $s\cdot\exp(0.000\,02s^2)/(Z_{Si} - f_{Si})(Z_{Cl} - f_{Cl})$, where $s = 4\pi/\lambda\cdot\sin(\theta/2)$ denotes the scattering variable (θ is the scattering angle and λ the de Broglie wavelength of the electrons), z_X is the atomic number and f_X the atomic scattering factor of element X

Each Me group was assumed to have local C_{3v} symmetry, with the C_3 axis coinciding with the adjacent C–Si or C–N bond. The torsion angles of the Me groups bound to the Si atoms were fixed with τ(H–C–Si–N) = 60° and that of the Me group bound to N (for **2** only) was fixed with τ(H–C–N–Si^1) = 30°. Overall, therefore, six and four independent torsion angles remained for compounds **1** and **2**, respectively.

The amplitudes of vibration (u) were either refined or, if not refinable, fixed at values calculated using the *ab initio* force field and the ASYM 40 program package (which is similar to ASYM 20).[16] Amplitudes calculated to be greater than 40 pm were fixed at 40 pm; interatomic distances with larger amplitudes of vibration do not contribute significantly to the experimental data.

---

§ Considering the *ab initio* calculated relative energies with zero-point energy (ZPE) correction for the conformational minima on the PES of compounds **1** and **2** (see Table 3), the diastereomeric composition at $T = 343$ K would be as follows: *meso*-**1** : *rac*-**1** = 0.62 : 1.00; *meso*-**2** : *rac*-**2** = 0.81 : 1.00. For the ED refinement, the experimentally obtained diastereomeric compositions (1 : 1 in each case) were used.

Table 2 Structural parameters obtained by gas-phase electron diffraction and *ab initio* geometries for six conformers, obtained at the MP2/6-31G* level[a]

(*a*) NH(SiHMeCl)$_2$ **1** (three conformers of *meso*- and three conformers of *rac*-**1**)

		MP2/6-31G*						
	ED	*meso*-**1A**	*meso*-**1B**	*meso*-**1C**	*rac*-**1A**	*rac*-**1B**	*rac*-**1C**	Average[b]
r_1(Si–N)	171.2(2)	173.5, 173.8	173.9	173.9	173.7, 174.0	173.6	173.7	173.7
r_2(N–H)	102.0[c]	101.9	102.0	102.0	102.0	101.9	101.8	101.9
r_3(Si–H)	148.8(17)	147.9, 148.1	147.8	148.1, 148.2	147.9, 148.2	147.8	148.1	148.0
r_4(Si–Cl)	206.2(1)	207.8, 207.7	207.4	207.4, 207.3	207.5, 207.3	207.7	207.7	207.6
r_5(Si–C)	184.5(3)	186.5, 186.3	186.6	186.6, 186.4	186.5, 186.3	186.5	186.4	186.4
r_6(C–H)	111.9(5)	109.4	109.4(1)[d]	109.4(1)[d]	109.4	109.4	109.4	109.4
a_1[e]	128.8(12)	129.1	128.0	131.5	129.2	127.6	131.3	129.5
a_2[f]	1.10[c]	115.6, 115.3	115.3	112.6, 114.1	114.3, 115.1	116.2	114.4	115.1
a_3(N–Si–Cl)	112.9(4)	111.5, 111.3	112.5	111.6, 111.2	112.2, 111.1	111.3	111.3	111.5
a_4(N–Si–H)	107.6[c]	108.1, 107.9	106.8	105.9, 108.8	108.8, 109.3	107.3	107.0	107.6
a_5(N–Si–C)	115.7(9)	110.4, 111.0	110.2	113.3, 110.7	109.3, 110.0	110.9	112.0	111.0
a_6(C–Si–Cl)	102.6(6)	107.6	107.1	106.8, 108.1	108.1, 108.5	107.3	107.3	107.5
a_7(C–Si–H)	113.5[c]	113.8, 113.6	113.9	112.0, 112.9	113.4, 113.2	114.0	113.2	113.5
a_8(Si–C–H)	110.8[c]	110.8(4)[d]	110.9	110.8(6)[d]	110.8(5)[d]	111.0	110.8(7)[d]	110.8
τ_1(Cl–Si–N–H)[g]	−85(8)	−91.1, −88.3						
τ_2(Cl–Si–N–H)[g]	−97(13)		−76.7, 76.7					
τ_3(Cl–Si–N–H)[g]	114(11)			105.4, −64.4				
τ_4(Cl–Si–N–H)[g]	−81(9)				−95.6, 62.2			
τ_5(Cl–Si–N–H)[g]	101(15)					−83.8		
τ_6(Cl–Si–N–H)[g]	102(4)						98.3	
τ_7(H–C–Si–N)[h]	60.0	61.7, 62.5	60.7, 59.4	55.1, 58.1	60.4, 60.2	61.7	58.3	60.4

(*b*) NMe(SiHMeCl)$_2$ **2** (four conformers; two most abundant conformers of *meso*- and *rac*-**2**)

		MP2/6-31G*				
	ED	*meso*-**2A**	*meso*-**2B**	*rac*-**2A**	*rac*-**2B**	Average[b]
r_1(Si–N)	171.5(1)	173.7, 173.6	173.7	173.8, 174.1	173.9, 173.5	173.7
r_2(N–C)	147.4(6)	148.2	148.3	148.3	148.1	148.2
r_3(Si–H)	145(2)	147.8, 148.2	147.8	147.8, 148.4	147.8	147.9
r_4(Si–Cl)	207.1(1)	207.9, 208.2	207.7	207.9, 207.7	207.9, 208.2	207.9
r_5(Si–C)	185.2(2)	186.6, 186.5	186.8	186.7, 186.4	186.7, 186.8	186.6
r_6(C–H)	113.4(3)	109.4(1)[d]	109.4(1)[d]	109.4(1)[d]	109.4(1)[d]	109.4
a_1[e]	124.9(6)	125.4	124.6	125.0	123.7	124.7
a_2[f]	1.2(5)	116.9, 117.5	117.5	117.9, 114.9	116.9, 119.1	117.3
a_3(N–Si–Cl)	108.3(5)	110.3, 111.0	111.1	111.9, 110.5	109.9, 110.8	110.8
a_4(N–Si–H)	107.7(10)	108.3, 107.4	107.7	108.2, 107.7	107.9, 107.5	107.8
a_5(N–Si–C)	115.1(8)	111.8, 113.0	111.3	111.4, 112.9	112.0, 112.7	112.1
a_6(C–Si–Cl)	107.3(7)	107.0, 107.6	106.5	107.0, 107.9	106.8, 106.5	107.0
a_7(C–Si–H)	110.0(14)	112.8	113.1	112.4, 112.9	113.1, 112.6	112.8
a_8(Si–C–H)	110.1(8)	110.8(10)[d]	110.8(4)[d]	110.8(10)[d]	110.8(4)[d]	110.8
a_9(N–C–H)	109.6(14)	110.7(8)[d]	110.9(2)[d]	110.7(9)[d]	110.8(9)[d]	110.8
τ_1(Cl–Si–N–C)[g]	−67.7(17)	−76.7, −78.1				
τ_2(Cl–Si–N–C)[g]	−72.4(9)		−68.8, 68.8			
τ_3(Cl–Si–N–C)[g]	−80.5(9)			−80.2, 60.4		
τ_4(Cl–Si–N–C)[g]	−84.4(9)				−74.0, −73.1	
τ_5(H–C–N–Si)	30.0	44.5	28.0	−44.0	41.3	43.4
τ_6(H–C–Si–N)[h]	60.0	−61.5, −51.4	60.0, 60.0	53.8, 58.8	60.0, 55.8	59.8

[a] Distances in pm, angles in °. Estimated standard deviations (e.s.d.s) are given in parentheses. The e.s.d.s for *ab initio*-calculated parameters denote more than two different values for this parameter, so that the arithmetic average and the e.s.d. are given. If two numbers are given for an *ab initio* calculated parameter, they refer to different values for the two SiHMeCl groups. [b] Population-weighted average of the *ab initio* values of all conformers. [c] Parameter fixed at values or averaged values calculated *ab initio*. [d] Averaged value and e.s.d. for parameter representing several slightly different bond lengths of the same type, whose average value is the same for both SiHMeCl groups. [e] For ED, a_1 refers to a_{av}(Si–N–Si); for *ab initio* it denotes a(Si–N–Si) of the single conformer. [f] For ED, a_2 refers to a_{diff}(Si–N–Si); for *ab initio* it denotes a(Si–N–C/H) of the single conformer. [g] Only one parameter was used to describe both Cl–Si–N–C/H torsions in a conformer. For details see text. [h] The ED parameter was fixed to obtain a staggered conformation of the Me group with respect to the Si–N bond as is suggested by *ab initio*-calculated values.

Refinement of the structure of compound 1

Fig. 1(*a*) shows the radial distribution curve (RDC) and Fig. 2(*a*) the observed molecular scattering curve of compound **1**. The RDC exhibits three peaks and two shoulders below 220 pm corresponding to six bonded distances. Owing to its low contribution to the scattering the N–H distance just gives rise to a shoulder at the left-hand side of the peak at 105 pm, so neither the bond length nor the vibrational amplitude could be refined; both were fixed at the values calculated *ab initio*. The major contribution to the peak at 105 pm comes from the C–H bonds. The bond length was refined using the *ab initio* derived values as additional observations (‘flexible restraints’) within the SARACEN method [see Table 4(*a*)].

The shoulder at 150 pm is caused by the Si–H bond distance, the peak at 180 pm contains contributions from the Si–C and Si–N bonds, while the most intense peak in the RDC at 210 pm is due to the Si–Cl bonds. These four latter distances were refined without any constraints or restraints, but their amplitudes were restrained according to Table 4(*a*). The values of r(C–H), r(Si–N), r(Si–C) and r(Si–Cl) differed markedly from those obtained by *ab initio* geometry optimisations (up to 2.5 pm, see Table 2) but are nevertheless reliable as they have

Table 3 *Ab initio*-calculated relative energies, E_{rel}/kJ mol^{-1}, dipole moments, μ/D, and relative abundances, x_i, of PES minima for *meso*-**1** and *rac*-**1** (MP2/6-311+G*-level) and *meso*-**2** and *rac*-**2** (MP2/6-31G*-level)

					x_i		
	τ_1, τ_2[a] (opt)	μ[b]	E_{rel}[c]	E_{rel} + ZPE[c]	293 K[d]	343 K[d]	ED[e]
meso-**1**							
Conformer **A**	−91.1, −88.3	1.25	0.25	0.29	0.348	0.325	0.325
B	−76.7, 76.7	4.02	3.85	3.85	0.081	0.090	0.090
C	105.4, −64.4	3.37	3.26	4.14	0.072	0.085	0.085
rac-**1**							
Conformer **A**	−95.6, 62.2	3.33	1.71	2.01	0.102	0.110	0.110
B	−83.8, −83.8	1.78	0.84	0.84	0.165	0.165	0.165
C	98.3, 98.3	0.60	0.00	0.00	0.233	0.225	0.225
meso-**2**[f]							
Conformer **A**	−76.7, −78.1	0.78	0.00	0.25	0.300	0.281	0.334
B	−68.8, 68.8	3.98	2.38	2.26	0.131	0.139	0.166
C	92.4, −59.4	3.33	4.31	3.85	0.069	0.080	—
rac-**2**[f]							
Conformer **A**	−80.2, 60.4	3.45	0.04	0.67	0.196	0.197	0.222
B	−74.0, −73.1	1.30	0.13	0.00	0.258	0.247	0.278
C	83.5, 85.5	0.26	3.68	4.22	0.046	0.056	—

[a] τ_1 and τ_2 denote the Cl–Si–N–X dihedral angles (X = H for **1** and C for **2**). For the *meso* diastereomers, the first one refers to the Si atom with *S* configuration and for the *rac* diastereomers it refers to the enantiomers in which both Si atoms have *S* configurations. [b] The calculated dipole moments for compounds **1** and **2** at 293 K are as follows (experimental values[7] in parentheses): **1**, 1.77 (2.27); **2**, 2.01 (2.59 D). [c] E_{rel} and E_{rel} + ZPE relative to conformer **C** of *rac*-**1**. [d] Under the experimental conditions, normalised to 0.5 for each diastereomer. [e] For the ED refinement, normalised to 0.5 for each diastereomer. For details see text. [f] E_{rel} relative to conformer **A** of *meso*-**2**, E_{rel} + ZPE relative to conformer **B** of *rac*-**2**.

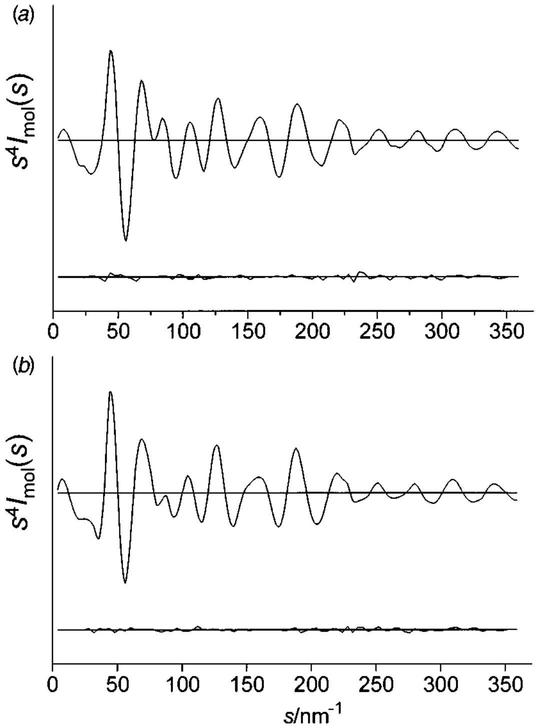

Fig. 2 Observed and final weighted difference combined molecular scattering curves for compounds **1** (*a*) and **2** (*b*). Theoretical data have been used for areas where no experimental data were available (0–20 and 356–360 nm^{-1}). I_{mol} denotes the molecular scattering intensity

Table 4 Flexible restraints used for the ED refinements. Values in parentheses denote the uncertainties attributed to the *ab initio* restraints

Parameter	*ab initio* Restraint	Refined value	Parameter	*ab initio* Restraint	Refined value
(*a*) NH(SiHMeCl)$_2$ **1**					
r_2/r_6	0.93(10)	0.91	u_2/u_3	0.82(8)	0.88
a_1	129.0(15)	128.8	u_2/u_6	0.92(9)	1.05
a_3/a_5	1.01(2)	0.98	u_8/u_9	0.92(9)	0.87
a_3/a_6	1.04(2)	1.10	u_{12}/u_{15}	0.76(8)	0.74
τ_1/τ_4	0.95(15)	1.08	u_{17}	32.0(30)	29.4
τ_2/τ_5	0.91(15)	0.95	u_{18}/u_{19}	1.63(8)	1.64
τ_3/τ_6	1.07(15)	1.14	u_{20}	27.0(30)	24.9
u_1/u_5	0.88(4)	0.93	u_{21}	40.0(40)	38.5
u_4	49.7(50)	53.7			
(*b*) NMe(SiHMeCl)$_2$ **2**					
r_6	108.5(20)	113.4	a_9	108.1(15)	109.4
a_1	125.5(10)	125.5	u_3	8.6(9)	9.4
a_2	1.0(5)	1.0	u_6	7.7(8)	7.5
a_4	108.4(10)	108.1	u_{17}	15.7(16)	13.9
a_5	113.1(10)	115.2	u_{20}	19.1(19)	18.6
a_7	112.1(15)	110.8	u_{25}	22.7(23)	22.3
a_8	111.6(15)	109.5			

relatively small estimated standard deviations (e.s.d.s). Important correlation (Table 5) for bonding distances and amplitudes occurs only between r_1(Si–N) and r_5(Si–C) and between their amplitudes and can be attributed to the fact that the Si–C and the Si–N bond give rise to the same peak in the RDC.

The most important contribution to the peak at about 250 pm comes from the H(C)Si distance, the amplitude of which could be refined without any constraint. The section from 265 up to *ca.* 350 pm arises from two-bond distances, *i.e.* mainly Si(N)Si, N(Si)Cl, N(Si)C and Cl(Si)C and two different Cl(SiC)H distances. Despite *ab initio*-derived restraints of the ratios a_3/a_5 and a_3/a_6, the N–Si–C angle refined to a much bigger and the C–Si–Cl angle to a much smaller value than calculated *ab initio*. Strong correlation in this region of the RDC occurs only between a_1(Si–N–Si)$_{av}$ and a_5(N–Si–C) and between u_8[N(Si)Cl] and u_9[N(Si)C]. However, not all parameters contributing to the shape of the radial distribution curve in this region could be refined, so it is possible that uncertainties of some angles are underestimated, and apparent differences between experimental and theoretical values may not be significant. The remaining part of the radial distribution curve can be separated into two parts, one between about 360 and 490 pm

Table 5 Least-squares correlation matrices (×100). Only absolute values ⩾30 are given

(*a*) NH(SiHMeCl)$_2$ **1**

	r_1	r_3	r_4	a_3	a_5	τ_1	τ_3	τ_5	τ_6	u_4	u_5	u_8	u_9	u_{12}	u_{16}	u_{18}	u_{21}	k_1	k_2
r_3	45																		
r_5	69	33																	−51
a_1				−52	−72													35	−34
a_5				41															
a_6				−31	−35														
τ_2						−52		55	−43						−41				
τ_4						37													
τ_5						−92			−42										
τ_6						43													
u_1			38								87							37	
u_5			49																
u_9												85							
u_{12}				−47								−59	−55						
u_{15}				−42								−51	−52	46					
u_{16}						35	39									31			52
u_{19}															32	93			
u_{20}																			
k_1										79									
k_2	−42													36					

(*b*) NMe(SiHMeCl)$_2$ **2**

	r_1	r_2	r_5	a_1	a_2	a_6	a_8	τ_1	τ_2	τ_3	τ_4	u_1	u_2	u_5	u_8	u_9	u_{12}	u_{16}	k_1	k_2
r_2	61		47																	
r_3	32												30							
r_4	−30	−74		53										−32						
r_5	65																			
r_6		53																		
a_1						−41					−31				36	39				
a_3						−35		−63	−72	−69	−44				−33	35	−43	−32		
a_5															59			57		33
a_6	−31		−32					32		49	37				−86	−53				
a_7																				34
a_9			42				40													
τ_1									40	54	44					−39	61			
τ_2					40					66	41							32		
τ_3											31				43	−46				
τ_4					54										−30	−39	40	39		
u_1			−36										63							
u_3	−41		−31									46							71	49
u_4	47		50									−39		−37						−45
u_5																				
u_8															53					
u_9															33					
u_{15}						44									−34			40		
u_{19}						30		30												
k_1												36								33
k_2	−62	−55	−51									38								

and one above 490 pm. Both depend entirely on the conformation, *i.e.* on the torsion angles τ_1 to τ_6. All Si(NSi)Cl and Si(NSi)C distances contribute to the former part, as do all Cl(SiNSi)Cl distances of conformers in which the two Cl atoms are on the same side of the SiNSi plane and a few Cl(SiNSi)C and C(SiNSi)C distances. All Cl(SiNSi)Cl distances with the two Cl atoms on different sides of the SiNSi plane and most of the Cl(SiNSi)C and C(SiNSi)C distances contribute to the part above 490 pm, the weight of their contribution naturally depending on the relative abundances of the appropriate conformers. All six torsion angles have rather big e.s.d.s, but adopt values more-or-less close to 90 or −90°. The physical meaning of this is discussed below. There is a very strong negative correlation between the torsion angles of *meso*-**1A** and *rac*-**1B** and also strong positive correlation between u_{18} and u_{19}, two vibrational amplitudes for different Si(NSi)C distances. The refined parameters and distances are given in Tables 2(*a*) and 6(*a*), respectively. The least-squares correlation matrix is presented in Table 5(*a*). Fig. 3 shows the six conformers of compound **1**, viewed along the $Si^1 \cdots Si^2$ axis.

Refinement of the structure of compound 2

Fig. 1(*b*) shows the RDC and Fig. 2(*b*) the observed molecular scattering curve of compound **2**. The part of the RDC between 100 and 240 pm is due to the six bonded distances and the one non-bonded N(C)H distance, giving rise to four peaks. Restraining r_6(C–H), u_3(Si–H) and u_6(C–H), all six bonded distances and the corresponding amplitudes of vibration could be refined to reasonable values with low e.s.d.s, except for r(Si–H). A negative correlation exists between r_2(C–N) and r_4(Si–H) and a positive one between r_1(Si–N) and r_5(Si–C), both cases due to similarity in bond length. The RDC region between 250 and 350 pm mainly shows the two-bond distances. The Si(C)H distance occurs, as for **1**, at about 250 pm, but gives only a shoulder of the peak at about 300 pm. Another shoulder of this peak, appearing at about 275 pm, is attributable primarily to two different Si(N)C distances and the H(Si)Cl distance. The peak at 300 pm has the same main contributors as for **1** but additionally contains all C(NSi)Cl, one Cl(SiNSi)C and most of the C(SiN)C distances, some giving rise to a shoulder on the right-hand side. For **2**, restraints were put on most of the bond angles, only a_3(N–Si–Cl) and a_6(C–Si–Cl) refining freely.

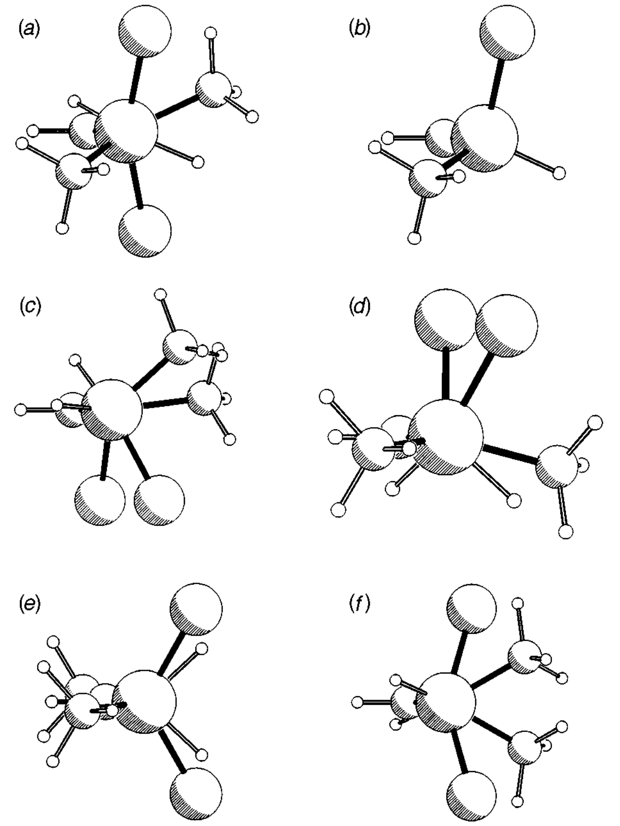

Fig. 3 Experimental conformers of compound **1**, projected along $Si^1 \cdots Si^2$ (Si^2 is obscured by Si^1): (*a*) *meso*-**1A**, (*b*) *meso*-**1B** (H^2, Cl^2 and $CH_3{}^2$ are obscured by H^1, Cl^1 and $CH_3{}^1$), (*c*) *meso*-**1C**, (*d*) *rac*-**1A**, (*e*) *rac*-**1B** and (*f*) *rac*-**1C**

In contrast to **1**, a_6(C–Si–Cl) refined nearly exactly to the *ab initio* value whereas angle a_5(N–Si–C) shows, despite restraints, a big difference. Surprisingly, given the large number of different distances in this area, only one strong correlation occurs, between u_8[N(Si)Cl] and a_6(C–Si–Cl).

The RDC region between 400 and 500 pm represents all Si(NSi)Cl distances, the two Cl(SiNSi)Cl distances for which both Cl atoms are on one side of the SiNSi plane, most of the Si(NSi)C, one Cl(SiNSi)C and a few C(NSi)C distances. The two Cl(SiNSi)Cl distances where both Cl atoms are on opposite sides of the SiNSi plane, together with most other five-bond distances, are the main contributors to the part of the RDC beyond 500 pm. All four torsion angles show the same tendency to adopt absolute values more-or-less close to 90° as was found for compound **1**, but with much smaller e.s.d.s. Strong correlation occurs between a_3(N–Si–Cl) and nearly all torsion angles and between τ_2 and τ_3. The refined parameters and distances are given in Tables 2(*b*) and 6(*b*), respectively. The least-squares correlation matrix is presented in Table 5(*b*). Fig. 4 shows the four conformers of **2**, viewed along the $Si^1 \cdots Si^2$ axis.

Discussion

The most striking feature of all conformers of compounds **1** and **2**, established by *ab initio* calculations as well as by analysis of the ED data, is the tendency of τ(Cl–Si–N–X) (X = H **1** or C **2**) to adopt absolute values close to 90°, *i.e.* for the Si–Cl bond to lie in a plane more-or-less orthogonal to the SiNSi plane. *Ab initio* geometry optimisations show that the deviation from orthogonality is smallest for the energetically most stable conformers (see Table 3). A second-order perturbation analysis for *rac*-**1C** in the natural bond orbital (NBO) basis[17] revealed two large 'donor–acceptor' interactions between the lone pair on the nitrogen atom and the σ^*(Si–Cl) orbital. According to a rough estimate based on the deletion of the corresponding Fock matrix elements, the sum of these interactions corresponds to *ca.* 89 kJ mol^{-1}. This energy is approximately four times as large as that of the n(N)–σ^*(Si–C) interaction. Additionally, if the geometry is optimised while deleting the n(N)–σ^*(Si–X) Fock matrix elements, the Si–Cl bonds move away from the orthogonal position. It thus seems very likely that n(N)–σ^*(Si–Cl) hyperconjugation determines the conformations of all isomers of **1** and **2**, as any overlap between the corresponding orbitals is greatest for an arrangement in which the Si–Cl bond is orthogonal to the SiNSi plane.

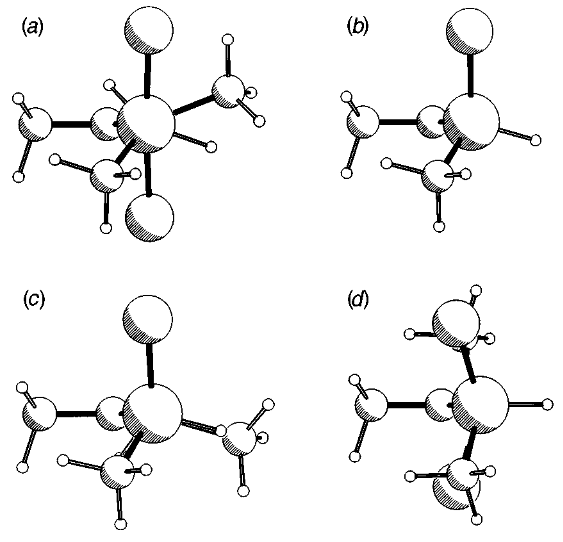

Fig. 4 Experimental conformers of compound **2**, projected along $Si^1 \cdots Si^2$ (Si^2 is obscured by Si^1): (*a*) *meso*-**2A**, (*b*) *meso*-**2B** (H^2, Cl^2 and $CH_3{}^2$ are obscured by H^1, Cl^1 and $CH_3{}^1$), (*c*) *rac*-**2A** and (*d*) *rac*-**2B**

The Si–N bond lengths of compounds **1** and **2** are very similar to those of $NH(SiHCl_2)_2$[6] and $NMe(SiHCl_2)_2$[6] and are about 1 pm shorter than those of $NH(SiHMe_2)_2$[2] and $NMe(SiHMe_2)_2$[4] (Table 7). The overall variations in this bond length in this group of compounds is rather small but our present investigations nevertheless show that a shortening of the Si–N bond occurs as soon as one methyl group on each Si atom is replaced by a Cl atom, with no effect on replacing the second methyl group. This observation corroborates the idea of n(N)–σ^*(Si–Cl) hyperconjugation since this involves only one Cl substituent on an Si atom, with a second one then not being in position for good overlap of its σ^*(Si–Cl) orbital with the lone pair of the nitrogen atom. The same tendency is observed for the series $NMe_2(SiH_{3-n}Cl_n)$ (n = 0–2) (see Table 7), with a much bigger effect on the Si–N bond length due to the fact that the orbital representing the lone pair is not 'shared' between two σ^*(Si–Cl) orbitals.

There are, of course, other forces influencing the Si–N torsion. Comparing *e.g.* the *ab initio* energies for the conformers of *rac*-**1** and *rac*-**2** (see Table 2), it is striking that *rac*-**1C** is the global energy minimum for **1**, while the conformationally similar *rac*-**2C** is the least favoured of the six conformers of **2**. It is likely that the more narrow Si–N–Si angle of **2**, caused by a repulsion between the *Si*-methyl and the *N*-methyl groups, with a consequently stronger repulsion of the two *Si*-methyl groups [see Fig. 3(*f*) for a picture of *rac*-**1C**] is responsible for the change in the order of relative energies. Nevertheless, many other starting conformations, including those in which the Si–C bonds are nearly orthogonal to the SiNSi plane, were used in *ab initio* geometry optimisations and all of them refined to one of the minima with nearly orthogonal position of the Si–Cl bonds and the SiNSi plane.

The Si–Cl bond length for compound **1** is significantly shorter than that of **2**, a difference that is not found experimentally for $NH(SiHCl_2)_2$ and $NMe(SiHCl_2)_2$, although it is predicted *ab initio*.[7] The distances r(Si–C) and r(C–H) are also shorter for **1** than for **2**, but because of the larger e.s.d.s these

Table 6 Experimental interatomic distances and amplitudes of vibration (r_a/u) (in pm)^{a}

(*a*) NH(SiHMeCl)$_2$ **1**

	Atom pair	*meso*-**1A**	*meso*-**1B**	*meso*-**1C**	*rac*-**1A**	*rac*-**1B**	*rac*-**1c**
r_{1}	N–Si^{b}	171.2, 3.9(3)					
r_{2}	N–H^{b}	102.0, 7.1^{c}					
r_{3}	Si–H^{b}	148.8, 8.1(7)					
r_{4}	Si–Cl^{b}	206.2, 5.4(1)					
r_{5}	Si–C^{b}	184.5, 4.2(3)					
r_{6}	C–H^{b}	111.9, 6.8(4)					
r_{7}	N(Si)H^{b}	258.7, 12.1^{c}					
r_{8}	N(Si)Cl^{b}	315.1, 6.6(6)					
r_{9}	N(Si)C^{b}	301.2, 7.6(12)					
r_{10}	Si(C)H^{b}	247.3, 10.3(9)					
r_{11}	Si(N)H	233.9, 10.8^{c}	233.2, 10.8^{c}	235.2, 10.8^{c}	233.9, 10.8^{c}	233.2, 10.8^{c}	235.2, 10.8^{c}
r_{12}	Si(N)Si	308.9, 11.7(12)	310.3, 11.7^{d}	306.0, 11.7^{d}	308.9, 11.7(12)	310.3, 11.7^{d}	306.0, 11.7^{d}
r_{13}	H(Si)Cl^{b}	281.5, 13.0^{c}					
r_{14}	H(Si)C^{b}	279.2, 12.1^{c}					
r_{15}	C(Si)Cl^{b}	305.5, 15.4(14)					
r_{16}	Si(NSi)Cl	427.8, 30(2)	424.2, 30^{d}	441.3, 30^{d}	445.8, 30^{d}	407.4, 30^{d}	417.4, 30^{d}
r_{17}	Si(NSi)Cl^{e}			399.1, 30^{d}	412.4, 30^{d}		
r_{18}	Si(NSi)C	367.5, 20(3)	464.0, 12.5^{d}	356.4, 12.5^{d}	361.4, 12.5^{d}	467.5, 12.5^{d}	366.2, 12.5^{d}
r_{19}	Si(NSi)C^{e}	461.5, 12.5(17)		378.6, 12.5^{d}	465.9, 12.5^{d}		
r_{20}	Cl(SiNSi)Cl	592.6, 25(3)	454.5, 25^{d}	442.8, 25^{d}	469.5, 25^{d}	532.6, 25^{d}	572.4, 25^{d}
r_{21}	Cl(SiNSi)C	428.4, 39(4)	593.3, 39^{d}	547.6, 39^{d}	432.8, 39^{d}	562.1, 39^{d}	403.7, 39^{d}
r_{22}	Cl(SiNSi)C^{e}	544.8, 39^{d}			598.2, 39^{d}		
r_{23}	C(SiNSi)C	547.5, 20.0^{f}	584.2, 20.0^{f}	348.5, 20.0	539.6, 20.0	596.0, 20.0	377.4, 20.0

(*b*) NMe(SiHMeCl)$_2$ **2**

	Atom pair	*meso*-**2A**	*meso*-**2B**	*rac*-**2A**	*rac*-**2B**
r_{1}	N–Si^{b}	171.5, 4.3(2)			
r_{2}	N–C^{b}	147.4, 5.2(6)			
r_{3}	Si–H^{b}	144.8, 9.2(8)			
r_{4}	Si–Cl^{b}	207.1, 5.3(1)			
r_{5}	Si–C^{b}	185.2, 5.3(2)			
r_{6}	C–H^{b}	113.4, 7.4(2)			
r_{7}	N(Si)H^{b}	255.9, 12.1^{c}			
r_{8}	N(Si)Cl^{b}	307.4, 9.2(13)			
r_{9}	N(Si)C^{b}	301.1, 8.1(16)			
r_{10}	Si(C)H^{b}	248.2, 11.9^{c}			
r_{11}	Si(N)C^{b}	272.1, 7.9(5)	273.8, 7.9^{g}	272.1, 7.9^{g}	273.8, 7.9^{g}
r_{12}	Si(N)Si^{b}	305.8, 11.5(12)	302.4, 11.5^{g}	305.8, 11.5^{g}	302.4, 11.5^{g}
r_{13}	H(Si)Cl^{b}	287.3, 13.0^{c}			
r_{14}	H(Si)C^{b}	271.4, 12.8^{c}			
r_{15}	C(Si)Cl^{b}	316.3, 8.1(8)			
r_{16}	Si(NSi)Cl	438.6, 15.6(10)	431.1, 31.2^{g}	425.1, 31.2^{g}	417.5, 15.6^{g}
r_{17}	Si(NSi)C	353.2, 14.0(11)	447.0, 14.0^{g}	356.8, 14.0^{g}	454.4, 14.0^{g}
r_{18}	Si(NSi)C^{e}	446.2, 14.0^{h}		454.4, 14.0^{h}	
r_{19}	C(NSi)Cl	358.0, 24(3)	365.6, 24^{g}	373.2, 24^{g}	380.0, 24^{g}
r_{20}	C(NSi)C	344.8, 17.0(18)	343.4, 17.0^{g}	334.4, 17.0^{g}	334.4, 17.0^{g}
r_{21}	C(NSi)C^{e}	435.3, 8.5^{i}		432.5, 17.0^{i}	
r_{22}	Cl(SiNSi)Cl	609.5, 7.0(7)	472.9, 7.0^{g}	450.8, 7.0^{g}	585.0, 7.0^{g}
r_{23}	Cl(SiNSi)C	477.6, 40.0^{c}	599.1, 40.0^{c}	373.2, 23.8^{c}	520.7, 40.0^{c}
r_{24}	Cl(SiNSi)C	516.5, 40.0^{c}		487.0, 40.0^{c}	
r_{25}	C(SiNSi)C	505.6, 22(2)	547.5, 22^{g}	505.4, 11^{g}	602.2, 11^{g}

[a] Estimated standard deviations obtained in least-squares refinements are given in parentheses. Other Cl···H, Si···H, N···H, C···H and H···H distances were included in the refinements, but are not listed. [b] Common distance and amplitude for all conformers. [c] Fixed to values obtained from *ab initio*-calculated force fields. [d] Amplitude refined for *meso*-**1A** and others tied to it. [e] Second distance of this type. Owing to symmetry constraints, identity to the first distance is possible for some conformers. [f] Refined in previous refinements but not included in the final one. [g] Amplitude tied to that for *meso*-**2A**. [h] Amplitude tied to u_{17} of *meso*-**2A**. [i] Amplitude tied to u_{20} of *meso*-**2A**.

differences are not significant. *Ab initio* calculations do not predict any of these differences, which may be due to shrinkage effects associated with the r_a structures. The Si–Cl bonds of **1** and **2** are longer than those in NH(SiHCl$_2$)$_2$ and NMe(SiHCl$_2$)$_2$ whereas their Si–C bonds are shorter than those of NH(SiHMe$_2$)$_2$ and NMe(SiHMe$_2$)$_2$. This is in accordance with observations for SiMe$_2$Cl$_2$,[20] SiMe$_3$Cl[21] and SiMe$_4$[22] showing a shortening of the Si–C and Si–Cl bonds on replacing Me groups by Cl atoms.

In the ED refinement of compound **1**, only three bond angles were refined and only one of them, a_3(N–Si–Cl), is in good agreement with the *ab initio* prediction. As restraints were used for a_5(N–Si–C) and a_6(C–Si–Cl) as well, we believe the differences between the *ab initio* and the ED results to be genuine. The experimental findings are consistent with an enhanced electronegativity difference between Si and C and Cl, respectively, which according to Bent's rule[23] should narrow the C–Si–Cl angle. This would also explain the shorter Si–C and Si–Cl bonds, but not the rather large N–Si–C angle, for which we do not have a plausible explanation at the present.

The smallest sums of angles around nitrogen according to MP2/6-31G* geometry optimisation are 358.2 (*meso*-**1C**) and 357.8° (*rac*-**2A**), so it proved to be reasonable to assume an overall planar Si$_2$NX configuration for all conformations of compounds **1** and **2**.

Finally, comparison of the experimental dipole moments[7] with the *ab initio* calculated ones (Table 3) gives an independent measure of how much the *ab initio* calculated geometries

Table 7 Distances (pm) and angles (°) for some silylamines

	r_a				
Compound	Si–N	Si–C	Si–Cl	Si–N–Si	Ref.
$NMe_2(SiH_3)$	171.3(5)				18
$NMe_2(SiH_2Cl)$	168.7(2)		207.0(1)		19
$NMe_2(SiHCl_2)$	168.1(4)		205.6(1)		19
$NH(SiH_3)_2$	172.5(3)			127.7(1)	1
$NH(SiHMe_2)_2$	172.7(3)	186.7(3)		130.4(15)	2
$NH(SiHMeCl)_2$	171.2(2)	184.5(3)	206.2(1)	129.2(12)*	This work
$NH(SiHCl_2)_2$	171.9(2)		204.1(1)	128.2(8)	6
$NMe(SiH_3)_2$	172.3(1)			125.2(2)	3
$NMe(SiH_2Me)_2$	171.8(3)	186.4(5)		125.6(10)	4
$NMe(SiHMe_2)_2$	172.7(4)	187.2(3)		126.1(5)	4
$NMe(SiHMeCl)_2$	171.5(1)	185.2(2)	207.1(1)	125.0(6)*	This work
$NMe(SiHCl_2)_2$	171.1(2)		204.0(1)	122.8(8)	6

* Population-weighted average over all conformers.

may apply to the conformers actually present and their relative energies. Since the computed dipole moments vary substantially between the various conformers, the averaged value calculated for the mixture is quite sensitive to the composition of the latter. For both compounds **1** and **2** calculated dipole moments are in each case about 0.5 D (22%) smaller than the experimental ones. Possible errors in the theoretical individual dipole moments notwithstanding, we still regard this to be a good agreement between experiment and theory, because the energy differences between the single conformers are small. The extent to which this structural analysis is capable of explaining the infrared spectra is discussed in ref. 7.

Conclusion

The main factor determining the conformation of chlorosilylamines seems to be $n(N)$–σ^*(Si–Cl) hyperconjugation. Other intramolecular interactions such as van der Waals attraction or steric repulsion play only a minor role but may change the sequence of relative energies in related compounds.

Acknowledgements

We thank the EPSRC for the provision of microdensitometer facilities at the Daresbury Laboratory and for research fellowships (P. T. B. and H. E. R., grant GR/K44411). We thank the Leverhulme Trust (H. F.) and the Fonds der chemischen Industrie (M. B.) for research fellowships. The work in Zürich has been supported by the Alfried-Krupp-Stiftung. The *ab initio* calculations were performed on IBM RS 6000 workstations of the Rechenzentrum der Universität Zürich and on the C4-cluster of the Eidgenössische Technische Hochschule Zürich.

References

1 D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, W. S. Sheldrick, B. J. Aylett, J. A. Ellis and J. J. Monaghan, *J. Chem. Soc. A*, 1969, 1224.
2 G. Gundersen and D. W. H. Rankin, *Acta Chem. Scand., Ser. A*, 1984, **38**, 647.
3 D. G. Anderson and D. W. H. Rankin, *J. Mol. Struct.*, 1989, **195**, 261.
4 G. Gundersen, D. W. H. Rankin and H. E. Robertson, *J. Chem. Soc., Dalton Trans.*, 1985, 191.
5 D. W. H. Rankin and H. E. Robertson, *J. Chem. Soc., Dalton Trans.*, 1983, 265.
6 H. Fleischer, D. Hnyk, D. W. H. Rankin, H. E. Robertson, M. Bühl and W. Thiel, *Chem. Ber.*, 1995, **128**, 807.
7 H. Fleischer, D. C. McKean, C. R. Pulham and M. Bühl, preceding paper.
8 A. J. Blake, P. T. Brain, H. McNab, J. Miller, C. A. Morrison, S. Parsons, D. W. H. Rankin, H. E. Robertson and B. A. Smart, *J. Phys. Chem.*, 1996, **100**, 12 280; P. T. Brain, C. A. Morrison, S. Parsons and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1996, 4589.
9 S. H. Bauer and K. Kimura, *J. Phys. Soc. Jpn.*, 1962, **17**, 300.
10 C. M. Huntley, G. S. Laurenson and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1980, 954.
11 S. Cradock, J. Koprowski and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **77**, 113.
12 A. S. F. Boyd, G. S. Laurenson and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **71**, 217.
13 A. W. Ross, M. Fink and R. Hilderbrandt, *International Tables for X-Ray Crystallography*, ed. A. J. C. Wilson, Kluwer, Dordrecht, Boston and London, 1992, vol. C, p. 245.
14 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
15 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.
16 L. Hedberg and I. M. Mills, *J. Mol. Spectrosc.*, 1993, **160**, 117.
17 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735; A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.
18 G. Gundersen, R. A. Mayo and D. W. H. Rankin, *Acta Chem. Scand., Ser. A*, 1984, **38**, 579.
19 D. G. Anderson, A. J. Blake, S. Cradock, E. A. V. Ebsworth, D. W. H. Rankin, H. E. Robertson and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1987, 3035.
20 R. L. Livingston and L. O. Brockway, *J. Am. Chem. Soc.*, 1944, **66**, 94.
21 R. L. Livingston and L. O. Brockway, *J. Am. Chem. Soc.*, 1946, **68**, 719.
22 H. O. Jenkins and L. O. Brockway, *J. Am. Chem. Soc.*, 1936, **58**, 2036.
23 H. A. Bent, *J. Chem. Phys.*, 1960, **33**, 1259.

Received 14*th November* 1997; *Paper* 7/08219C