The Molecular Structures and Conformations of Bis(dichlorosilyl)amine and Bis(dichlorosilyl)methylamine in the Gas Phase: Determination by Electron Diffraction and by ab Initio Calculations

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The gas-phase molecular structures of bis(dichlorosilyl)amine, $(HSiCl_2)_2NH$, and bis(dichlorosilyl)methylamine, $(SiHCl_2)_2NMe$, have been investigated by electron diffraction and ab initio calculations on a MP2/6-31G* level. Because the latter suggest the presence of a mixture of two conformers for each molecule, attempts were made to fit the electron diffraction data in each case by two different models, one assuming the presence of only one conformation, and another allowing for two different conformers. The principal parameters (r_a) from electron diffraction for $(HSiCl_2)_2NH$ are (the appropriate ab initio calculated values are given in brackets [ ]): r(Si–N) 171.9(2) [172.7], r(Si–Cl) 204.1(1) [204.5] pm; Si–N–Si 126.5(8) [127.4], N–Si–Cl 107.3(5) [110.8] and Cl–Si–Cl 106.5(3) [107.5]°. For $(SiHCl_2)_2NMe$: r(Si–N) 171.1(3) [171.5], r(Si–Cl) 204.0(9) [205.2], r(N–C) 149.7(10) [148.3] pm; Si–N–Si 124.9(13) [123.4], N–Si–Cl 109.7(5) [110.7] and Cl–Si–Cl 107.1(3) [107.2]°. For $(HSiCl_2)_2NH$ three different conformers were found to fit the experimental data with the single-conformation model. In two of the conformers, the dichlorosilyl groups are twisted by Θ_1 = 146.0(10)/Θ_2 = 155.2(20)° and Θ_1 = 101.1(49)/Θ_2 = 196.8(12)° respectively counterclockwise from the positions in which the Si–H bonds eclipse the N–H bond. Both of these lead to nearly ideally staggered conformations of the two $SiHCl_2$ groups when viewed along the Si···Si axis. In contrast, the third conformation is nearly eclipsed, with torsion angles Θ_1 = 131.4(15)/Θ_2 = 80.4(26)°. Planarity of the Si_2NH group was assumed as suggested by ab initio calculation. For $(HSiCl_2)_2NMe$ the experimental data could be suitably fitted by two conformers, in which the dichlorosilyl groups are twisted by Θ_1 = 161.8(13)/Θ_2 = 63.1(23)° and Θ_1 = 156.1(9)/Θ_2 = 177.1(15)° from the positions in which the Si–H bonds eclipse the N–C bond. The first of these structures has an eclipsed Si(NSi)Cl conformation and an Si···Cl nonbonded distance close to the sum of the appropriate van der Waals radii. MP2/6-31G* calculations support the GED bond lengths and bond angles of both molecules, but indicate different conformations for the most stable equilibrium geometries: the computed twists are Θ_1 = 180/Θ_2 = 180° and Θ_1 = 177.0/Θ_2 = 183.0° for $(HSiCl_2)_2NH$ and $(HSiCl_2)_2NMe$, respectively. Rotation about the Si–N bonds is a very facile process, cf. the computed [MP2/6-31G*//MP2/6-31G* + ZPE(SCF/6-31G*)] rotational barrier of 2.9 kJ · mol^{-1} for $(HSiCl_2)_2NH$.

Tertiary amines, R_3N, and secondary amines, R_2NH, almost exclusively exhibit pyramidal configurations (triisopropylamine, $(Me_2CH)_3N$, is an example of a tertiary amine with a planar configuration[1]). In contrast, tri- and disilylamines show trigonal planar coordination at the nitrogen atom. The Si–N–Si angles in disilylamines are larger than 120°, the exact value depending on the third substituent on N. This observation can be explained by hyperconjugation, i.e. interaction between the p type lone pair on N and Si–X σ^* (antibonding) orbitals, which is favoured by such geometrical arrangements, whereas in the case of aliphatic amines[2] such interactions are much less significant. As a consequence Si–N bonds are strengthened and shortened, especially in compounds bearing further electronegative groups at the Si atom. This has been shown convincingly for the series Me_2NSiH_2X (X = H, Me, Cl, Br, I)[3,4].

Gas-phase structures have been reported for many disilylamines[5–11], but none of them contains a halogenated silicon atom. It was therefore of interest to determine the gas-phase structures of the title compounds and to compare their principal structural parameters with those of the methylated and hydrogenated disilylamines.

Another objective of the investigation was to see whether the conformations of the title compounds are similar to those of $(HSiMe_2)_2NH$[6] and $(HSiMe_2)_2NMe$[9]. Disilylamines with N–H bonds and some disilylethers[12] tend to have conformations determined more by minimisation of the interactions between the groups bound to the different silicon atoms than by the interactions between Si- and N-substituents. Me and Cl are similar in their van-der-Waals radii but different in their electronic properties. This should

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lead to similar conformations if van-der-Waals potentials predominate but to different structures if electrostatic or dipole-dipole interactions are more significant.

Experimental and Computational Section

A sample of $(HSiCl_2)_2NH$ was prepared by reaction of $CaCl_2 \cdot 8\ NH_3$ with an excess of $HSiCl_3$ at 233 K in *n*-pentane solution[13], and $(SiHCl_2)_2NMe$ was prepared by reaction of NH_2Me with an excess of $HSiCl_3$ also in *n*-pentane solution at 253 K[14]. Both compounds were purified by fractional distillation. Purities were checked by Differential Scanning Calorimetry.

Electron-diffraction scattering intensities were recorded on Kodak Electron Image plates, using the Edinburgh diffraction apparatus[15,16] with nozzle-to-plate distances of 95 and 256 mm and an accelerating voltage of 44.5 kV. During exposures the nozzle was maintained at 326/331 K for $(HSiCl_2)_2NH$ (sample temperature 303 K) or at 337/341 K for $(HSiCl_2)_2NMe$ (sample temperature 318 K). 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[17]. 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[17] and least-squares refinement programs[18]. 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[19].

Table 1. Weighting functions, correlation parameters and other experimental data

Compound	$(HSiCl_2)_2NH$		$(HSiCl_2)_2NMe$	
Camera height/mm	95.12	255.86	95.51	255.70
Electron wavelength/pm	5.700	5.700	5.700	5.700
Δs/nm^{-1}	4	2	4	2
s_{min}/nm^{-1}	120	20	120	20
sw_1/nm^{-1}	140	40	140	40
sw_2/nm^{-1}	304	140	304	140
s_{max}/nm^{-1}	356	172	356	164
p/h[a]	0.099	0.466	-0.158	0.464
Scale factor k	0.845(22)	0.847(10)	0.770(21)	0.777(11)

[a] Correlation parameter.

The ab initio calculations were performed on IBM RS 6000 workstations of the Rechenzentrum der Universität Zürich and on the C4-cluster of the ETH Zürich. Geometry optimisations were performed using standard methods and a 6-31G* basis set[20] with the GAUSSIAN92 program package[21] (five d-functions were used). Initially, the optimisations started from the experimental, refined coordinates and were carried out in C_1 symmetry without any constraints. Analytic frequencies were obtained at the HF/6-31G* level followed by reoptimisation at the correlated MP2/6-31G* level. The MP2/6-31G* parameters are included in Table 2.

Since the optimised conformations were found to diffe from those of the GED refinements, a detailed study of th conformational part of the PES (potential energy surface of $(HSiCl_2)_2NH$ (in terms of dihedral angles about th N−Si-bonds) was undertaken at the SCF/6-31G* level. Fo fixed H−Si−N−H torsional angles, Θ_1 and Θ_2, the remaining geometrical parameters were optimised. Θ_1 and Θ_2 wer each varied in steps of 30 degrees form 0 to 360. Two minima were located, and the transition structure between thes two was optimised at the SCF/6-31G* and MP2/6-31G* levels. Unless otherwise noted, energies are reported at th MP2/6-31G*//MP2/6-31G* level including SCF/6-31G* zero point corrections (ZPE), scaled by 0.89[20].

Table 2. Geometrical parameters (distances/pm; angles/°)[a]

Parameter		$(HSiCl_2)_2NH$		$(HSiCl_2)_2NMe$	
		GED	MP2/6-31G*	GED	MP2/6-31G*
r_1	Si-N	171.9(2)	172.7	171.1(2)	171.5
r_2	Si-Cl	204.1(1)	204.5	204.0(1)	205.2
r_3	Si-H	145.2(23)	147.0	143.2(34)	145.4
r_4	N-H/N-C	102.1[b]	102.1	149.7(10)	148.3
r_5	C-H			112.8(21)[b]	108.2
a_1	Cl-Si-Cl	106.6(3)	107.5	107.1(3)	107.2
a_2	N-Si-Cl	107.3(5)	110.8	109.7(5)	108.7(1)[c]
a_3	N-Si-H	108.4[b]	108.4	110.2[b]	110.2
a_4	Si-N-Si	126.5(8)[c]	127.4	124.9(13)	123.4
a_5	H-C-N			110.5[b]	110.5(2)[c]
a_6	N-C-dip[d]			0.0[b]	-3.9
a_7	Si-N twist[d]	146.0(10)	180.0	161.8(13)	177.0
a_8	Si-N twist[d]	155.2(20)	180.0	63.1(23)	183.0
a_9	C-N-twist[d]			-10.0[b]	32.1
a_{10}	Si-N-H/C	116.8(8)	116.3	117.5[e]	118.2
a_{11}	H-Si-Cl[c]	113.5	109.7	109.9	108.9(2)[c]

[a] Experimental parameters are r_a, computed ones r_e. Estimated standard deviations obtained in the least-squares refinements are quoted in parentheses. – [b] Fixed. – [c] Different values were calculated for molecular parameters set equal in the GED-refinement. The mean values and the estimated standard deviations are given. – [d] For definition, see text. – [e] Dependent parameter.

Results

Molecular Models: For both molecules, two different models were used for refinement: In the first, only one conformer was allowed to be present whereas the second model allowed for two conformers. In the latter, all corresponding bond lengths and angles except for Si−N−Si were assumed to be equal. In the case of Si−N−Si, the arithmetic average for both conformers and half of the difference were chosen as independent parameters. The difference parameter could not be refined, but an acceptable value was found by performing a series of refinements with it fixed at various values. The parameter defining the mole fractions of the two conformers was not refined but was also studied by performing a series of refinements with different values and subsequently fixing it at the value which gave the lowest *R*-factor.

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 and to have local C_s symmetry. Planarity at nitrogen was assumed for the $(HSiCl_2)_2NH$ model, with both Si−N−H angles being equal, thus leaving only one independent angle at nitrogen. In the case of $(HSiCl_2)_2NMe$, both C−N−Si angles were set equal and the deviation from planarity was defined by a dip-angle between the N−C bond and the bisector of the Si−N−Si angle. This parameter was not refined but fixed by a plot of the R-factor against the dip-angle. The angles at silicon were defined by N−Si−Cl, N−Si−H and Cl−Si−Cl for all models.

The overall conformations adopted by the molecules were described in terms of torsional angles (Θ), i.e. H−Si−N−H for $(HSiCl_2)_2NH$ and H−Si−N−C for $(HSiCl_2)_2NMe$. In each case, the arrangement with the Si−H bond eclipsing the N−H/N−C bond was taken as the origin and positive values were given to counterclockwise rotations.

For the $(HSiCl_2)_2NMe$ model, the N−Me group was assumed to have local C_{3v} symmetry. The conformation of the methyl group was defined by the dihedral angle H−C−N−Si(1), with zero twist for the conformation in which one H−C bond eclipsed the N−Si(1) bond.

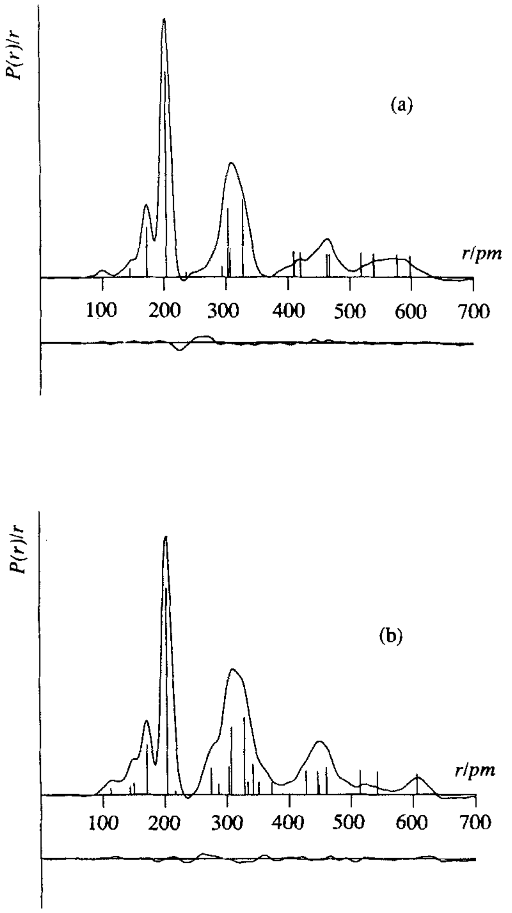
There were, therefore, two and three independent torsional angles for $(HSiCl_2)_2NH$ and $(HSiCl_2)_2NMe$, respectively, within the single-conformer model. These numbers were doubled with the two-conformer model, i.e. four torsional angles for $(HSiCl_2)_2NH$ and six for $(HSiCl_2)_2NMe$.

The amplitudes of vibration (u) were either refined or, if not refinable, fixed at values calculated using the ab initio force-field results as input for the ASYM40 program package (which is similar to ASYM20[22]). Amplitudes calculated to be greater than 40 pm were fixed at 40 pm, as larger values do not contribute to the experimental data.

Refinement of the Structure of $(HSiCl_2)_2NH$: The radial distribution curve, Figure 1(a), shows four peaks below 230 pm corresponding to the four bonded distances. Although there is a clearly separated peak at 100 pm the corresponding N−H distance and vibrational amplitude could not be refined and had to be fixed at the ab initio calculated value. The other three peaks correspond to Si−H, Si−N and Si−Cl bonded distances, the last one being the biggest peak. The Si−H bond length could not be refined in the early stages and converged to a rather small value during the last refinements, together with a refined amplitude which was much smaller than the calculated value. The Si−N and Si−Cl bond lengths refined very easily with small standard deviations and their amplitudes of vibration could be refined without any constraint. The latter did not differ so much from the calculated values as was the case for u(Si−H), but showed some correlation [as shown in the least-squares correlation matrix, Table 3(a)].

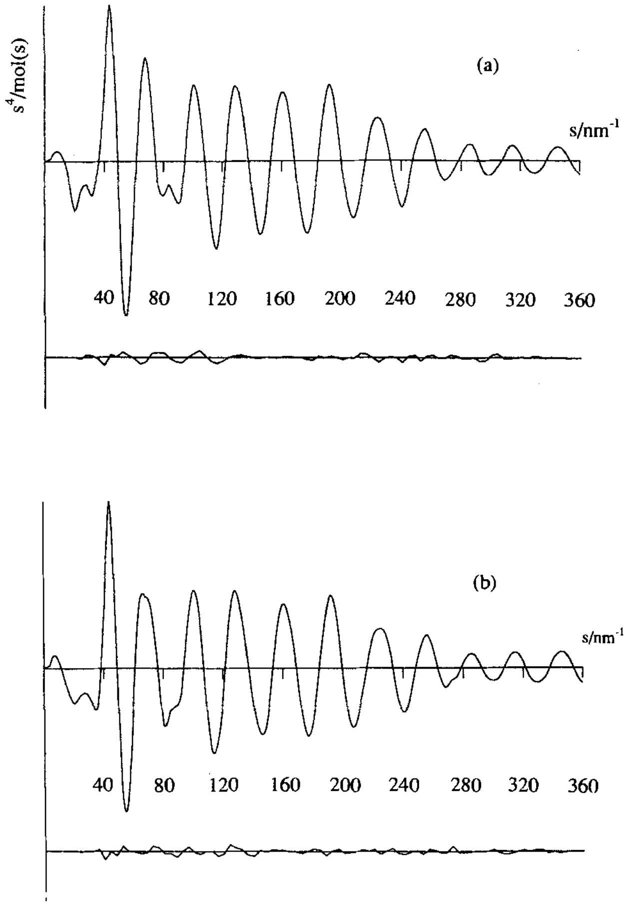
The H(N)Si distances contribute little to the curve and their peak at about 235 pm is partially covered by that of the Si−Cl pairs. The section from 250 up to ca. 370 pm arise from two-bond distances, i.e. mainly Si(N)Si, N(Si)Cl and Cl(Si)Cl. The radial distribution curve contains only one peak for all three distances, with Si(N)Si and N(Si)Cl close together and Cl(Si)Cl giving rise to the shoulder on the right-hand side. There is almost no correlation between the N−Si−Cl and Cl−Si−Cl angles, but a large correlation is found for the N−Si−Cl and H−N−Si angles because the latter is determined mainly by the Si(N)Si, rather than the H(N)Si, distance [(H−N−Si) = (π-(Si−N−Si)/2)]. One of the two other conformers, which were found, (later referred to as conformer B), also contributes an Si(NSi)Cl distance to this region. The H(Si)N atom pairs give rise to a small shoulder on the left side: the H−Si−N angle could not be refined and so its value was fixed as calculated ab initio.

Figure 1. Observed and final difference radial distribution curves, $P(r)/r$ for (a) $(HSiCl_2)_2NH$ and (b) $(HSiCl_2)_2NMe$. Before Fourier inversion the data were multiplied by $s \cdot \exp[0.00002 \cdot s^2/(Z_{Si} - f_{Si})(Z_{Cl} - f_{Cl})]$



The remaining part of the radial distribution curve depends entirely on the conformation, i.e. on the torsional angles Θ_1 and Θ_2. The Si(NSi)Cl distances, depending either on Θ_1 or on Θ_2, are mainly responsible for the region between 400 and 500 pm. In the case of the highest possible symmetry, C_{2v}, this region should contain only one peak. If C_2 or C_s symmetry is assumed, there should be two different maxima. Conformations with C_1 symmetry give rise to four more-or-less distinguishable peaks, except for the special case in which the Si−N−Si plane bisects one Cl−Si−Cl

Figure 2. Observed and final weighted difference combined molecular scattering curves for (a) $(HSiCl_2)_2NH$ and (b) $(HSiCl_2)_2NMe$. The curves for $(HSiCl_2)_2NH$ relate to conformer A, that for $(HSiCl_2)_2NMe$ to conformer D



angle, for which three maxima are exhibited. The peaks between 500 and 600 pm are attributable to the Cl(SiNSi)Cl distances. There must be two different maxima for C_{2v} symmetry, three for C_s and C_2 symmetry and four in the case of C_1 symmetry, although there may be some overlap. Within the single-conformer model all special cases were studied systematically. In addition, the torsional angles were examined separately, i.e. one of them remained fixed while the other one was varied. During this procedure three different conformations, with *R*-factors of 0.0688, 0.0693 and 0.0706 were obtained. The first of these, subsequently referred to as conformer A, exhibits nearly C_2 symmetry [Θ_1 = 146.0(10), Θ_2 = 155.2(20)°], the second, referred to as conformer B, exhibits no symmetry except C_1 [Θ_1 = 131.4(15), Θ_2 = 80.4(26)°], and the same is true for conformer C [Θ_1 = 101.1(49), Θ_2 = 196.8(12)°]. Conformers A and C show a staggered conformation along the Si···Si axis, whereas conformer B leads to a nearly eclipsed arrangement. The *R*-factor ratio of conformer B and A (1.0073), the number of data-points (133), taken as the number of independent observations, and the difference in the number of refining parameters (3), taken as the degrees of freedom were used as input data for the Hamilton test[23]. This statistical test gives the degree of confidence to which the hypothesis, that conformer B is the correct one, can be rejected. The value in the appropriate Hamilton table at the 50%-confidence level for the conditions given above is 1.010, thus bigger than the *R*-factor ratio. Therefore, the hypothesis, that conformer B is the correct one, cannot be rejected at this level. The *R*-factor ratio of conformer C and conformer A is equal to 1.0262, the difference in the number of refining parameters is 2 and again the number of data points is 133. The Hamilton values for these conditions are 1.025 and 1.031 at the 95%- and 97.5% confidence level, respectively. Thus, the hypothesis, that conformer C is the correct one, can be rejected with more than 95% confidence.

Table 3. Least-squares correlation matrices × 100[a]. – (a) $(HSiCl_2)_2NH$, conformer A; (b) $(HSiCl_2)_2NMe$, conformer D

(a)

	a_{10}	u_2	u_6	u_8	u_{17}	u_{19}	u_{20}	u_{21}	u_{22}	u_{23}	u_{24}	k_1
a_1	-52			-50								
a_2	63		59	57					-54			
a_7										50		
a_8					-59			-71				
a_{10}			64	73								
u_1		67										73
u_2												92
u_6				85								
u_{17}							-57					
u_{18}						-57		64				
u_{22}											51	

(b)

	r_3	r_4	a_4	u_2	u_3	u_8	u_{13}	u_{17}	u_{18}	k_1
r_1	50				63					
r_3		-65			81					
r_4			65		-72					
a_1							60			
a_2			-74			-64				
a_4						65				
a_7									64	
a_8								-52		
u_1				72						78
u_2										92
u_{17}									63	

[a] Only elements with absolute values >50 are listed; k_i are defined in Table 1, a_i in Table 2 and u_i in Table 4.

Within the two-conformer model, all three possible binary mixtures (A + B, A + C, B + C) were investigated with mole fractions equal to 0.2, 0.4, 0.6 and 0.8. In no case did one of the mixtures result in a significantly lower *R*-factor compared to those resulting from the single-conformer model, nor could the minimum value for the mole fraction be determined reliably. On the other hand, as all three conformers fit the data almost equally well, any mixtures of them cannot be excluded on the basis of the GED data.

With the torsional angles fixed to the ab initio values (180/180° and 180/0°), a refinement was done within the two-conformer model. The minimum in the plot of *R*-factor against the mole fraction (m.f.) of the 180/180° conformer resulted for m.f. = 0.35, compared to the ab initio calcu-

Table 4. Experimental interatomic distances (r_a/pm) and amplitudes of vibration (u/pm)[a]

Atom pair	$(HSiCl_2)_2NH$		$(HSiCl_2)_2NMe$	
	Distance	Amplitude	Distance	Amplitude
r_1 N-Si	171.9(2)	4.1(3)	171.1(3)	4.0(4)
r_2 Si-Cl	204.1(1)	4.8(1)	204.0(1)	4.7(1)
r_3 Si-H	145.2(17)	6.3(17)	143.2(34)	7.1(24)
r_4 N-H/N-C	102.0	7.1[b]	149.7(10)	3.5(tied to u_3)
r_5 C-H			112.8(21)	7.5[b]
r_6 Cl(Si)Cl	327.1(5)	10.5(5)	328.2(5)	9.1(3)
r_7 H(Si)Cl	293.8(16)	14.0[b]	288.5(25)	12.2[b]
r_8 Si(N)Si	307.0(10)	6.4(3)	303.3(18)	9.1(4)
r_9 N(Si)Cl	303.4(10)	12.8(tied to u_7)	307.1(8)	9.1(tied to u_8)
r_{10} N(Si)H	257.6(14)	12.0[b]	258.7(28)	11.6[b]
r_{11} Si(N)H/C	236.1(6)	12.0[b]	274.5(7)	7.1(6)
r_{12} N(C)H			216.7(19)	9.9[b]
r_{13} $C^{10}(NSi^2)Cl^4$			372.0(22)	26.2(28)
r_{14} $C^{10}(NSi^2)Cl^5$			333.5(28)	26.2(tied to u_{13})
r_{15} $C^{10}(NSi^6)Cl^8$			448.2(10)	12.0(tied to u_{18})
r_{16} $C^{10}(NSi^6)Cl^9$			350.9(31)	26.2(tied to u_{13})
r_{17} $Si^6(NSi)Cl^4$	410.1(13)	33(12)	427.7(16)	14.5(25)
r_{18} $Si^6(NSi)Cl^5$	467.6(6)	21.2(50)	460.0(11)	12.0(11)
r_{19} $Si^2(NSi)Cl^8$	463.3(10)	9.5(8)	341.8(25)	26.2(tied to u_{13})
r_{20} $Si^2(NSi)Cl^9$	420.5(24)	26.6(72)	446.1(19)	12.0(tied to u_{18})
r_{21} $Cl^4(SiNSi)Cl^8$	518.5(31)	54(25)	460.2(46)	40.0[b]
r_{22} $Cl^4(SiNSi)Cl^9$	576.8(24)	17.4(21)	606.3(10)	12.1(10)
r_{23} $Cl^5(SiNSi)Cl^8$	598.3(30)	22.8(29)	514.7(38)	49.9(68)
r_{24} $Cl^5(SiNSi)Cl^9$	538.9(26)	17.2(19)	542.3(31)	49.9(tied to u_{23})

[a] Estimated standard deviations obtained in least-squares refinements are given in parentheses. Other Cl···H, Si···H, C···H and H···H distances were included in the refinement, but are not listed here. – [b] Fixed.

Table 5. Distances [pm] and angles [°] for some silylamines

Compound	r_a(Si-N)	r_a(Si-C)	r_a(Si-Hal)	r_a(Si···Si)	Si-N-Si	Ref.
Me_2NSiH_3	171.3(5)					3
Me_2NSiH_2Me	171.5(6)	186.7(6)				3
$Me_2NSiHMe_2$	171.9(5)	186.9(3)				3
Me_2NSiMe_3	171.0(5)	186.8(4)				26
Me_2NSiH_2Cl	168.7(2)		207.0(1)			4
Me_2NSiH_2Br	168.4(4)		224.9(2)			4
Me_2NSiH_2J	167.0(2)		244.6(3)			4
$Me_2NSiHCl_2$	168.1(4)		205.6(1)			4
$HN(SiH_3)_2$	172.5(3)			309.7(6)	127.7(1)	5
$HN(SiHMe_2)_2$	172.7(3)	186.7(3)		313.6(21)	130.4(15)	6
$HN(SiHCl_2)_2$	171.9(2)		204.1(1)	307.0(10)	128.2(8)	this work
$HN(SiMe_3)_2$	173.8(5)	187.6(1)		317(1)	131.3(15)	7
$MeN(SiH_3)_2$	172.3(1)			305.9(2)	125.2(2)	8
$MeN(SiH_2Me)_2$	171.8(3)	186.4(5)		305.7(8)	125.6(10)	9
$MeN(SiHMe_2)_2$	172.7(4)	187.2(3)		307.9(7)	126.1(5)	9
$MeN(SiHCl_2)_2$	171.1(2)		204.0(1)	303.3(18)	122.8(8)	this work
$MeN(SiMe_3)_2$	171.9	187.5(3)		310.8(2)	129.4(6)	10

lated composition of 43% 180/180° and 57% 180/0°. Nevertheless, even at this point, the *R*-factor only dropped to a value *R* = 0.1031. This is significantly higher than was obtained in the best refinement of the ED data, but it must be remembered that the electron diffraction (r_a) structure represents distances averaged over all atomic motions, some of which have large amplitudes in this case.

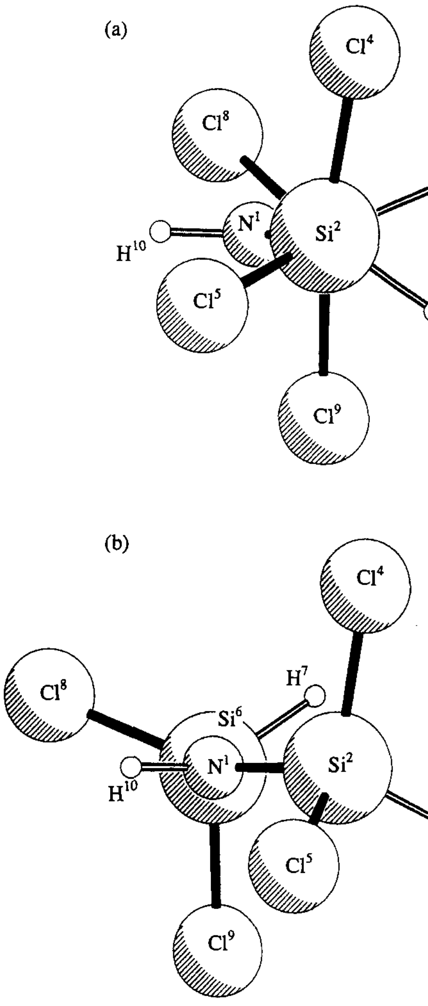
Since there were no important differences in the bond distances and valence angles only the final results of the slightly favoured conformation A resulting from the single-conformer model are presented in Tables 2–4. The refined parameters and distances are given in Table 2 and Table 4, respectively. The least-squares correlation matrix for refinement A is presented in Table 3(a). Observed and final weighted difference molecular scattering intensities are presented in Figure 2(a). Figures 3, 4 and 5 each show two different views of conformations A, B and C, respectively.

Refinement of the Structure of $(HSiCl_2)_2NMe$: The radial distribution curve, Figure 1(b), is qualitatively similar to that of $(HSiCl_2)_2NH$, but with some marked differences in the conformational region. The part of the curve between 100 and 230 pm, which is due to the five bonding distances, shows clearly four peaks. Since the Si–H and C–N distances give a common peak, both amplitudes of vibration had to be tied together and refined as a single parameter. A significant negative correlation was found between the N–Si–Cl and Si–N–Si angles [see Table 3(b)]. Each of the two parameters could be varied by nearly 5° without causing a significant change in the *R*-factor. Consequently the minimum which was finally found for these parameters is a shallow one. The *R*-factor plot for the dip angle leads to a minimum for planarity at the N atom, so this arrangement was therefore imposed by setting the dip angle to zero.

In comparison with the radial distribution curve for $(HSiCl_2)_2NH$, that for $(HSiCl_2)_2NMe$ has an additional peak at 275 pm originating from the C(N)Si distances. Some torsion-dependent Si···H and Cl···H distances also contribute to the region below 300 pm. In the refinement leading to conformer D of $(HSiCl_2)_2NMe$, one nonbonded Si···Cl distance is much smaller and one C(NSi)Cl distance larger than 400 pm (Table 4). The other three Si(NSi)Cl distances give rise to peaks between 400 and 500 pm, overlapping with the C(NSi)Cl distances between 340 and 450 pm. Finally, the Cl(SiNSi)Cl contributions are all above 450 pm, the longest distance being found at 606 pm. For $(HSiCl_2)_2NMe$ two distinct conformers with reasonable parameters and acceptable *R*-factors were found. The final refinement within the single-conformer model gave torsional angles Θ_1 = 161.8(13) and Θ_2 = 63.1(23)° with R_G = 0.0703 for conformer D and Θ_1 = 156.1(9) and Θ_2 = 177.1(15)° with R_G = 0.0720 for conformer E. The H–C–N–Si torsion could not be refined and was fixed at a value, determined by a plot of *R*-factor against this torsional angle. Even if conformer E is much more similar to the ab initio optimised conformation (Θ_1 = 177.0, Θ_2 = 183.0°), the hypothesis that this is the only conformer present can be rejected on the basis of the significance test[23] with more than 97.5% confidence (see refinement of $(HSiCl_2)_2NH$ for a more detailed description of this test). As for $(HSiCl_2)_2NH$, a mixture of conformers D and E was investigated within the two-conformer model, but no significant minimum could be found by variation of the mole fraction from 0.0 to 1.0 in steps of 0.2.

Ab initio calculations showed a second minimum in the Si–N torsional PES of $(HSiCl_2)_2NMe$, with Θ_1 = 15.7 and Θ_2 = 172.5°. This stationary point is, on a MP2/6-31G* level, 5.0 kJ mol^{-1} higher in energy than the 177/183° minimum. Thus, the composition calculated for the experimental temperature (see Experimental and Computational section) is 85% and 15% for the 177/183° and 16/173° minima, respectively. As for $(HSiCl_2)_2NH$, the two ab initio minimum geometries were, with fixed torsional angles, tested to fit the ED data within the two-conformer model. A plot of the R-factor against the mole fraction of conformer 177/183° results in a minimum $R = 0.1182$ for m.f. = 0.6. This value is again significantly higher than that in the best refinement of the ED data, but the same considerations as for $(HSiCl_2)_2NH$ have to be kept in mind.

Figure 3. (a) Experimental conformer A of $(HSiCl_2)_2NH$; projection along $Si^2 \cdots Si^6$ (Si^6 is obscured by Si^2) and (b) experimental conformer A of $(HSiCl_2)_2NH$; projection along N^1-Si^6 bond

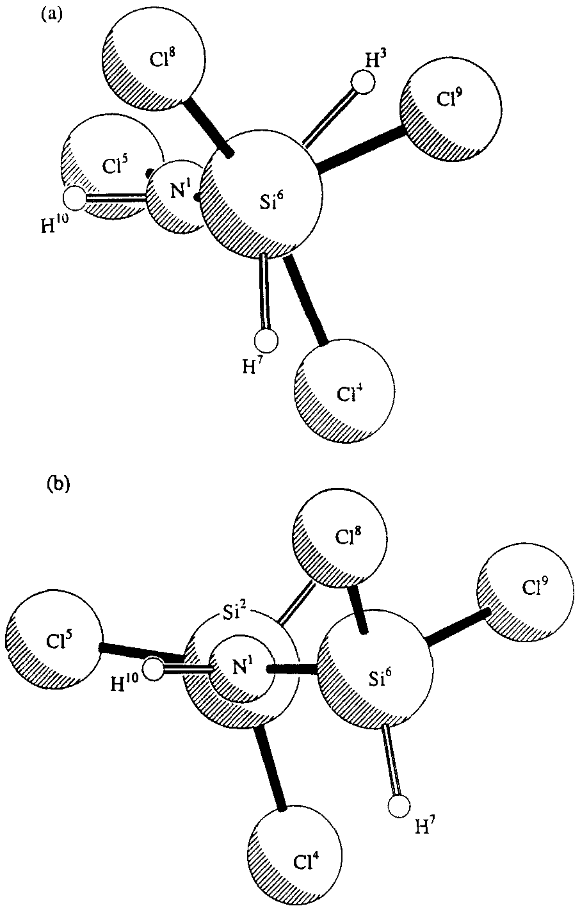


Discussion

Compared with $(HSiMe_2)_2NH$ and $(HSiMe_2)_2NMe$, $(HSiCl_2)_2NH$ and $(HSiCl_2)_2NMe$ do not show any significant changes in the Si–N bond distances (see Table 5). In disilylamines, therefore, replacement of methyl groups on silicon by chlorine atoms does not lead to shortening of the Si–N bonds, in contrast to the situation in monosilylated amines. This reflects the fact that the lone pair of electrons on the nitrogen atom is interacting with two silyl groups in disilylamines thus giving a weaker interaction between nitrogen and each silicon.

The Si–Cl bonds are of similar length in both molecules and are within the normal range. The Cl···Cl one-angle distances are about 328 pm for both molecules, but the Si···Si separations are different in the two cases. For $(HSiCl_2)_2NH$, $r(Si \cdots Si)$ is 307.0(5) pm, a value which is similar to that found for $(H_3Si)_2NH$, but smaller than those in $(HSiMe_2)_2NH$ and $(Me_3Si)_2NH$ (see Table 5). In $(HSiCl_2)_2NMe$, $r(Si \cdots Si)$ is 303.3(17) pm, a distance that is short compared with those in related N-methyldisilylamines, and is associated with a narrower Si–N–Si angle. A possible explanation for this will be given later.

Figure 4. (a) Experimental conformer B of $(HSiCl_2)_2NH$; projection along $Si^6 \cdots Si^2$ (Si^2 is obscured by Si^6) and (b) experimental conformer B of $(HSiCl_2)_2NH$; projection along N^1-Si^2 bond



As the results for $(HSiCl_2)_2NMe$ and the ab initio calculation show, it proved to be reasonable to assume a planar Si_2NH configuration for $(HSiCl_2)_2NH$ as well. The MP2/6-31G* geometry optimisation gave sums of angles around nitrogen of 360.0 and 359.9° for $(HSiCl_2)_2NH$ and $(HSiCl_2)_2NMe$, respectively. Additionally, there is no large out-of-plane vibration which might lead to a shrinkage effect on Si···C or Si···Si interatomic distances. In accord with the observations of Bürger[24] and Gundersen[9], two silyl substituents on nitrogen are sufficient to ensure planarity.

Nevertheless it should be mentioned that $(H_2SiPh)_2NOMe$ is found to exhibit a pyramidal configuration at the N-atom in the crystalline state[25].

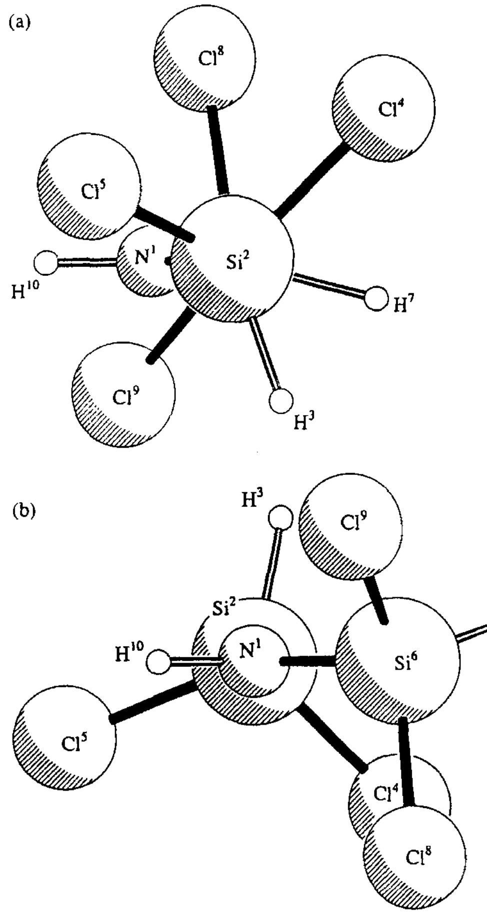


Figure 5. (a) Experimental conformer C of $(HSiCl_2)_2NH$; projection along Si^2···Si^6 (Si^6 is obscured by Si^2) and (b) experimental conformer C of $(HSiCl_2)_2NH$; projection along N^1−Si^2 bond

For $(HSiCl_2)_2NH$ three structures with different twist angles were found to fit the experimental data. Conformer A shows nearly perfect C_2 symmetry (Figure 3) and is basically the same structure that was found for $(HSiMe_2)_2NH$, with Cl instead of Me[6]. Therefore, it fits the conformational concepts for disilylethers and disilylamines with N−H bonds[9] as does conformer C (Figure 5). According to this principle, repulsions of groups bound to different Si atoms are the strongest interactions between non-bonded groups and thus force conformations which are staggered when viewed along the Si···Si axis.

In contrast, conformer B does not show a staggered but a nearly eclipsed conformation (Figure 4), similar to those adopted by conformer D of $(HSiCl_2)_2NMe$ and $(HSiMe_2)_2NMe$[9]. The fact that all three conformers of $(HSiCl_2)_2NH$ fit the experimental data well does not mean that they are all present in the gas phase (cf. refinement section). The shape of the $\tilde{\nu}$(Si−H) peak ($\tilde{\nu}$ = 2247 cm^{-1}) in the gas-phase IR-spectrum of $(HSiCl_2)_2NH$[13] indicates the presence of only one conformer, in which both Si−H bonds have similar environments. Due to this fact and on the basis of the *R*-factors of the last refinements we prefer conformation A. On the other hand, the possibility that there is a mixture of conformers present cannot be completely excluded, as the calculated energy difference between the conformers is rather small and stretching frequencies for different conformers could by chance be equal. According to the shallow PES, large-amplitude torsional vibrations are possible, so that the structure which is supported by the ED data need not be the only one that is actually present. In addition, it should always be kept in mind that GED and ab initio calculations refer to different types of geometries, namely r_a and r_e, respectively. The corresponding parameters associated with large-amplitude motions may differ to a larger extent than is usually the case.

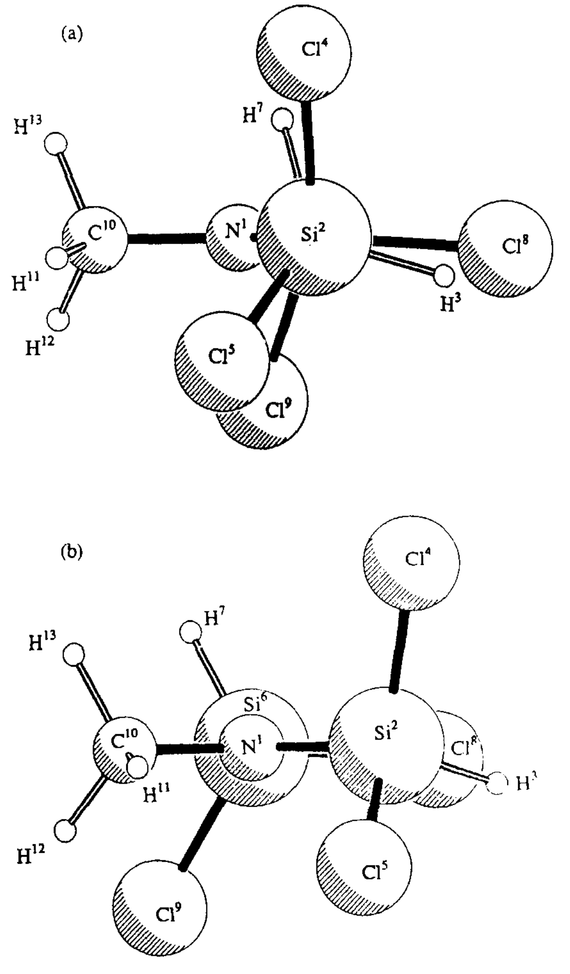


Figure 6. (a) Experimental conformer D of $(HSiCl_2)_2NMe$; projection along Si^2···Si^6 (Si^6 is obscured by Si^2) and (b) experimental conformer D of $(HSiCl_2)_2NMe$; projection along N^1−Si^2 bond

One important feature of the eclipsed conformation (D) of $(HSiCl_2)_2NMe$ is a non-bonded Si(NSi)Cl distance of 342 pm, which is close to the sum of the appropriate van-der-Waals radii[26]. In this conformer one Si(NSi)Cl torsion is nearly perfectly eclipsed, so that the Si···Cl nonbonded distance is close to its conformational minimum (Figure 6). The associated Cl···Si−Cl angle is about 140°. This structural behaviour can be explained by attractive forces between Si and Cl. Silicon, as an element of the second long period, can form hypervalent compounds and chlorine easily acts as a Lewis base. The rather narrow Si−N−Si angle is consistent with this interpretation. However, the rather weak, long-range Si···Cl interaction is not expected, nor observed to lead to any significant change in the Si−Cl bond length.

Figure 7. (a) Experimental conformer E of $(HSiCl_2)_2NMe$; projection along $Si^2 \cdots Si^6$ (Si^6 is obscured by Si^2) and (b) experimental conformer E of $(HSiCl_2)_2NMe$; projection along N^1-Si^2 bond

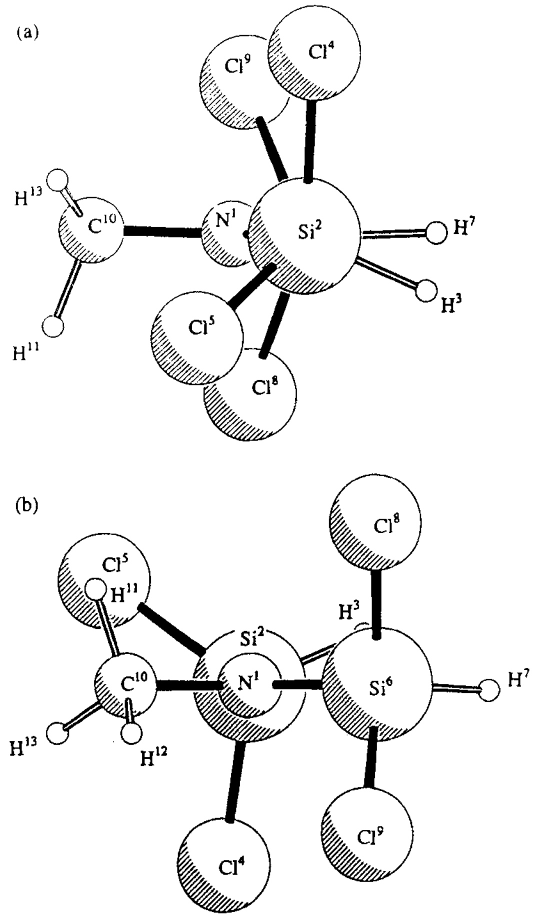
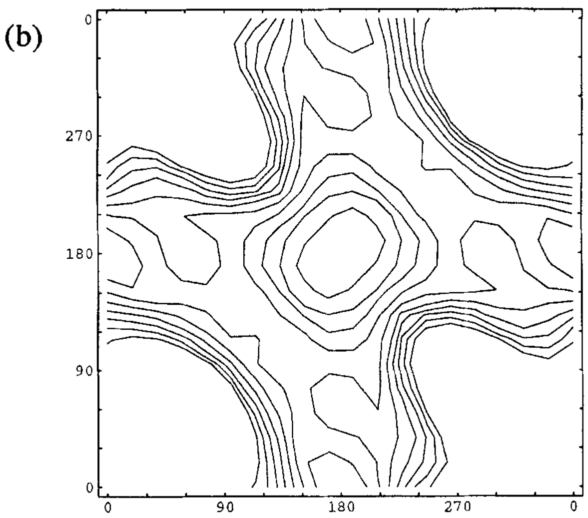


Figure 8. Potential energy (SCF/6-31G*) of $(HSiCl_2)_2NH$ as a function of the two H−N−Si−H torsional angles, Θ_1 and Θ_2. (a) Three-dimensional plot (relative energies in kcal mol^{-1}): the grid points with Θ-values of 0, 30, 60, etc. have been calculated (all other geometrical parameters optimised) and the others have been linearly interpolated and (b) contour plot of the PES: energy contours are at 0.2, 0.4, 0.6 etc. kcal mol^{-1} (1 kcal = 4.18 kJ). The points at Θ_1/Θ_2 = 180/180° and at Θ_1/Θ_2 = 180/0° are minima

(a)



The chemistry of $(HSiCl_2)_2NMe$[14] shows that transfer of a Cl atom between Si atoms is possible and conformer D would offer an ideal geometry for an intramolecular mechanism of such a reaction step.

It is possible that the N−Si−Cl angles in any one molecule are not all equal, but electron diffraction data do not provide information on such small deviations from idealised symmetry. The MP2/6-31G* optimised N−Si−Cl angles deviate somewhat more from the corresponding GED value for $(HSiCl_2)_2NH$ (Δ = 3.5°) than they do for $(HSiCl_2)_2NMe$ (Δ = 1.0°). The ab initio geometries of $(HSiCl_2)_2NMe$ also exhibit slightly different N−Si−Cl angles, which deviate by about 0.1° from the mean value (see Table 4). On the basis of the *R*-factors, conformer D (Figure 6) is slightly favored, even if conformer E (Figure 7) is closer to the ab initio calculated minimum. Of course, a mixture of conformers could be present in this case, too.

For both $(HSiCl_2)_2NH$ and $(HSiCl_2)_2NMe$, the ab initio optimised conformations at the MP2/6-31G* level differ notably from the structure refined using the GED data (see Table 2), whereas at the HF/6-31G* level $(HSiCl_2)_2NH$ does not have C_{2v} symmetry and its structure is quite close to that observed experimentally. For $(HSiCl_2)_2NH$ we therefore studied that part of the PES which describes the rotations about the Si−N bonds. The relative energies (SCF/6-31G* level) as a function of Θ_1 and Θ_2 are depicted in Figure 8. Two minimum energy conformations are apparent, namely at Θ_1/Θ_2 = 180/180° and at Θ_1/Θ_2 = 180/0°, with symmetries of C_{2v} and C_s, respectively. As expected, the PES is very flat, particularly near the C_{2v} form: changes of Θ_1 by as much as 30° cost less than 1 kJ mol^{-1} in energy. In fact, a very small imaginary frequency ν = 4i cm^{-1} is computed for the C_{2v} symmetry at SCF/6-31G*. This disappears at the correlated MP2/6-31G* level (smallest frequency 5 cm^{-1}). While the C_s minimum is 2.1 kJ/mol above the C_{2v} form at SCF/6-31G*, this value drops to 1.0 kJ mol^{-1} at MP2/6-31G*//MP2/6-31G* + ZPE. The transition structure between C_{2v} and C_s has C_1 symmetry (one imaginary frequency, ν = 16i cm^{-1}, SCF/6-31G*) with Θ_1/Θ_2 = 138/62° (SCF values, MP2//6-31G*: 137/60°), and is 3.8 kJ mol^{-1} above the C_{2v} form (SCF/6-31G*). Inclusion of electron correlation and ZPE reduces this barrier to 2.9 kJ mol^{-1}, suggesting very facile rotation about the Si–N bonds. The torsional angles show, that its conformation is similar to that of conformer B resulting from the ED data.

In summary, the conformational PES of $(HSiCl_2)_2NH$ is very flat, suggesting very facile rotation about the Si–N bonds. Temperature-dependent ^{1}H-NMR spectra[13] support this assumption.

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