Isopropyldisilylamine and Disilyl-t-butylamine: Preparation, Spectroscopic Properties, and Molecular Structure in the Gas Phase, determined by Electron Diffraction

David G. Anderson and David W. H. Rankin *
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The compounds $NPr^i(SiH_3)_2$ and $NBu^t(SiH_3)_2$ have been prepared by the gas-phase reactions of SiH_3Cl and the appropriate primary amines, and characterised by i.r. and n.m.r. spectroscopy. The molecular structures of both compounds in the gas phase have been determined by electron diffraction. In each case the bonds to nitrogen are coplanar. The most important parameters (r_a) for $NPr^i(SiH_3)_2$ are Si–N 172.7(1), C–N 148.7(5), and C–C 155.0(6) pm, and angles SiNSi 121.6(2), NCC 111.4(9), and CCC 107.6(15)°. The isopropyl group is twisted so that the unique C–H bond almost eclipses one of the Si–N bonds, and the asymmetry thereby introduced leads to non-equivalence of the SiNC angles, which are 121.9(5)° on the more crowded side and 116.5(5)° on the other side of the molecule. Principal parameters for $NBu^t(SiH_3)_2$ are Si–N 173.5(1), C–N 147.9(8), and C–C 154.6(4) pm, SiNSi 118.4(4) and NCC 109.2(6)°. In this case the butyl group has greatly compressed the SiNSi angle.

As part of a systematic study of compounds containing silicon–nitrogen bonds, we have determined the molecular structures of silylamines. The effects of changing the substituents on silicon in dimethyl(silyl)amines [1,2] and methyldisilylamines [3,4] are now well documented, but little attention has been paid to the consequences of changing the nitrogen substituents, other than simply replacing methyl groups by hydrogen.[4,5] We have therefore made a study of the structures of the four disilylamines $NR(SiH_3)_2$, R = Me, Et, Pr^i, or Bu^t, to see whether changing the *N*-alkyl group had any significant electronic or steric effects. The results of our work on the *N*-methyl and *N*-ethyl compounds have been published elsewhere,[6] and we now report the structures of the *N*-isopropyl- and *N*-t-butyl-amines.

Experimental

Volatile compounds used in the course of this work were handled in Pyrex glass vacuum lines fitted with greased taps. I.r. spectra were recorded using a Perkin-Elmer 598 spectrometer and a 10-cm gas cell which was fitted with KBr plates. N.m.r. spectra were recorded on Bruker WH360, WP200, and WP80 spectrometers using 5-mm glass tubes and deuteriated solvents to provide lock signals.

Preparation of Isopropyldisilylamine.—This amine was prepared by a method which is essentially the same as that used for other alkyldisilylamines.[7] Isopropylamine (15 mmol) was allowed to expand from a glass bulb (250 cm^3) into a second bulb (1 000 cm^3) which contained chlorosilane (10 mmol). Reaction was apparent from the formation of white isopropylammonium chloride. After addition of the amine was complete, the volatile products were removed and separated by fractional condensation *in vacuo*. Isopropyldisilylamine was obtained in 96% yield as the fraction which was retained in a trap held at 227 K. It was a colourless liquid.

Preparation of Disilyl-t-butylamine.—The reaction was essentially identical to that described above, with the replacement of isopropylamine by t-butylamine. Disilyl-t-butylamine was retained in a trap held at 227 K as a colourless liquid, and was obtained in 89% yield. The fraction passing the trap at 227 K included a component which appeared from its i.r. spectrum to be the secondary amine, $NHBu^t(SiH_3)$. This suggests that steric factors affect the ease with which two silyl groups can be accommodated around a nitrogen atom which already carries a bulky substituent.

Electron Diffraction.—Electron-diffraction scattering intensities were recorded on Kodak Electron Image photographic plates using the Edinburgh gas diffraction apparatus,[8] operating at *ca.* 44.5 kV. Three plates were recorded for each compound at each of the two camera distances (128 and 286 mm), and in all experiments the samples and nozzle were maintained at room temperature, 295 K. Optical densities of plates were obtained in digital form using a computer-controlled Joyce-Loebl MDM6 microdensitometer [9] at the S.E.R.C. Daresbury Laboratory. The programs used to control the scanner,[9] for data reduction,[9] and for least-squares analysis [10] have all been described previously. Standard scattering factors [11] were used in all calculations.

Details of the *s* ranges of the data, and weighting points, used in setting up the off-diagonal weight matrices used in the least-squares refinements are given in Table 1, with other pertinent experimental data. The electron wavelengths and camera

Table 1. Weighting functions, correlation parameters, scale factors, and wavelengths

Compound	Camera height/mm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor (k)	Wavelength/pm
		nm^{-1}							
$NPr^i(SiH_3)_2$	128.3	4	60	80	292	340	0.223	0.775(18)	5.674
	285.8	2	20	40	120	140	0.461	0.830(12)	5.673
$NBu^t(SiH_3)_2$	128.3	4	72	92	292	344	0.062	0.807(27)	5.672
	285.9	2	20	40	124	146	0.482	0.762(18)	5.674

Table 2. I.r. spectra/cm^{-1}

NPr^i(SiH$_3$)$_2$	NBu^t(SiH$_3$)$_2$
2 966s	2 965s
2 926m	2 931m
2 873m	2 880m
2 180s	2 181s
2 140vs	2 142vs
1 462m	1 474 ⎫
	1 466 ⎭m
1 389 ⎫	1 394m
1 380 ⎬m	
1 370 ⎭	1 368s
1 323w	
1 154s	1 198s
1 128m(sh)	
1 022s	1 049m
990s	999vs
958vs(sh)	971s
938 ⎫	942vs
932 ⎭vs	
906m(sh)	
870 ⎫	
865 ⎬m	
860 ⎭	810w
720s	723s
560w	555vw
453w	

s = Strong, m = medium, w = weak, v = very, and sh = shoulder.

Table 3. N.m.r. parameters

	N[C'H'(CH$_3$)$_2$](SiH''$_3$)$_2$	N[C'(CH$_3$)$_3$](SiH''$_3$)$_2$
δ(^{1}H)/p.p.m.	1.20	1.33
δ(^{1}H')/p.p.m.	3.29	
δ(^{1}H'')/p.p.m.	4.32	4.38
δ(^{13}C)/p.p.m.	23.5	30.8
δ(^{13}C')/p.p.m.	49.6	52.3
δ(^{29}Si)/p.p.m.	−48.8	−50.6
^1J(CH)/Hz	125.6	125.5
^1J(C'H')/Hz	135.3	
^1J(SiH'')/Hz	208.7	207.6
^2J(C'H)/Hz	2.2	n.r.
^2J(CH')/Hz	3.1	
^3J(CH)/Hz	4.8	4.4
^3J(C'H'')/Hz	2.2	n.r.
^3J(SiH')/Hz	3.0	n.r.
^3J(SiH'')/Hz	6.6	n.r.

n.r. = Not resolved. All spectra were recorded using CCl$_3$D as solvent, lock, and internal reference. Chemical shifts are relative to SiMe$_4$. Proton spectra were recorded at 80.13 MHz, ^{13}C spectra at 90.56 MHz, and ^{29}Si spectra at 71.55 MHz.

distances given in this table were determined by analysis of scattering patterns for benzene, which were recorded on the same occasions as the plates for the amines were exposed. The benzene data were analysed in exactly the same way as those for the amines, and systematic errors are thereby minimised. We believe that errors in wavelengths and camera distances do not contribute significantly to the overall errors in geometrical parameters.

Results

Preparation and Spectroscopic Characterisation.—The formation of isopropyldisilylamine and disilyl-t-butylamine in high yields is to be expected, but the observation of some butylmonosilylamine indicates that steric factors can influence reactivities even when only one bulky group is present. The two new amines were characterised by i.r. and n.m.r. spectroscopy. Details of the gas-phase i.r. spectra are given in Table 2. There are peaks in the regions expected for stretching and deformation modes of CH$_3$ and SiH$_3$ groups, and others which may be associated with skeletal modes, but we have not attempted to make definitive assignments.

Details of the n.m.r. spectra are presented in Table 3. The ^{1}H n.m.r. spectrum of NPr^i(SiH$_3$)$_2$ consisted of three groups of resonances. A singlet with ^{29}Si satellites was assigned to the SiH$_3$ group protons, and a doublet and septet were attributable to the protons of the isopropyl group. The ^{13}C n.m.r. spectrum showed more complex multiplets, with a quartet of quartets of doublets assigned to the methyl carbon atoms and a doublet of 13 lines assigned to the methine carbon, which coupled equally to methyl and silyl group protons. The ^{29}Si n.m.r. spectrum appeared to be a quartet of overlapping doublets of quartets, in which case the couplings would be ^1J(SiH), and two three-bond couplings, to the methine proton and to the other three SiH$_3$ protons. However, it is possible that the pattern could be a quartet of overlapping doublets of septets, with some lines lost in the noise, in which case the last splitting would be with the methyl group protons.

The ^{1}H n.m.r. spectrum of NBu^t(SiH$_3$)$_2$ consisted of two singlets, and the ^{29}Si n.m.r. spectrum was a quartet of broad lines. The ^{13}C n.m.r. spectrum contained two groups of resonances, a quartet of septets from the methyl group carbon atoms, and a broad group with unresolved couplings from the quaternary carbon. In both cases therefore the n.m.r. spectra provide strong evidence for the identities of the compounds, and the absence of additional resonances demonstrates the purity of the samples.

Structural Analysis.—*Molecular models.* When describing the geometries of NPr^i(SiH$_3$)$_2$ and NBu^t(SiH$_3$)$_2$ it was assumed that all SiH$_3$ and CH$_3$ groups had local C_{3v} symmetry. For each molecule the geometry at nitrogen was defined by Si–N and C–N distances, the angle SiNSi, and a dip angle, which was taken to be the angle between the C–N bond and the SiNSi plane. These dip angles were found to be zero at early stages in the refinements, and thereafter this was assumed.

In the case of the isopropylamine, the low symmetry of the alkyl substituent could lead to non-equivalence of the SiNC angles, and so an extra parameter, called the Si$_2$N wag, was introduced. This was defined as the angle between the SiNSi bisector and the C–N bond, in the plane of the heavy atoms. The final refined value of −2.7(5)° corresponds to a difference of 5.4° between the two SiNC angles, with the larger angle on the same side of the molecule as the two CH$_3$ groups, *i.e.* the more crowded side.

The twist angle about the C–N bond in NPr^i(SiH$_3$)$_2$ was defined relative to the position in which the unique C–H bond lay in the plane perpendicular to the SiNSi plane. A value of 90° therefore corresponds to the conformation in which this C–H bond eclipses one of the Si–N bonds, and the molecular skeleton has C_s symmetry, provided the bonds to nitrogen are coplanar. The observed conformation, with a twist angle of 76°, is close to this. The zero twist positions for the methyl groups in both compounds were defined to represent staggered conformations. The zero positions for parameters describing torsions about the Si–N bonds were taken to be those in which one Si–H bond of each group eclipsed the C–N bond. The two Si–N twist angles could be constrained to be equal, giving the N(SiH$_3$)$_2$ group

Table 4. Molecular parameters

		$\text{NPr}^i(\text{SiH}_3)_2$	$\text{NBu}^t(\text{SiH}_3)_2$
P_1	r(Si-N)	172.7(1)	173.5(1)
P_2	r(C-N)	148.7(5)	147.9(8)
P_3	r(C-C)	155.0(6)	154.6(4)
P_4	r(Si-H)	147.1(6)	150.1(8)
P_5	r(C-H)	113.6(3)	111.9(4)
P_6	SiNSi	121.6(2)	118.4(4)
P_7	NCC	111.4(9)	109.2(6)
P_8	HSiN	109.0(fixed)	109.0(fixed)
P_9	HCC	109.0(fixed)	109.4(16)
P_{10}	CCC	107.6(15)	109.8(6)[a]
P_{11}	NCH	109.0(fixed)	
P_{12}	Si_2N dip	0.0(fixed[b])	0.0(fixed)
P_{13}	C-N twist	75.9(5)	0.0(fixed[b])
P_{14}	Si-N twist	43.1(fixed[b])	20.8(91)
P_{15}	C-C twist	−5.3(fixed[b])	18.1(29)
P_{16}	Si_2N wag	−2.7(5)	0.0(fixed)
P_{17}	SiNC[a]	116.5(5)	120.8(2)
P_{18}	SiNC[a]	121.9(5)	

[a] Dependent parameter. [b] Varied earlier, see text.

Table 5. Least-squares correlation matrices × 100*

(*a*) $\text{NPr}^i(\text{SiH}_3)_2$

P_4	P_6	P_7	P_{10}	P_{16}	u_1	u_2	u_7	k_1	k_2	
	−55									P_1
−58	76									P_2
		−60		−63	−74	−95	−64		−64	P_3
			−83	73		60	58			P_7
						63	83			P_{16}
						80		76	63	u_1
							64	55	66	u_2

(*b*) $\text{NBu}^t(\text{SiH}_3)_2$

P_3	P_6	P_{15}	u_1	u_2	u_6	u_7	u_{15}	k_1	k_2	
—78	85			−76						P_2
	−67	65		80						P_3
				64						P_6
							67			P_7
									−72	P_9
						−57				P_{15}
								57		u_1
			70							u_2
					60					u_7

* Only elements with absolute values > 50 are included.

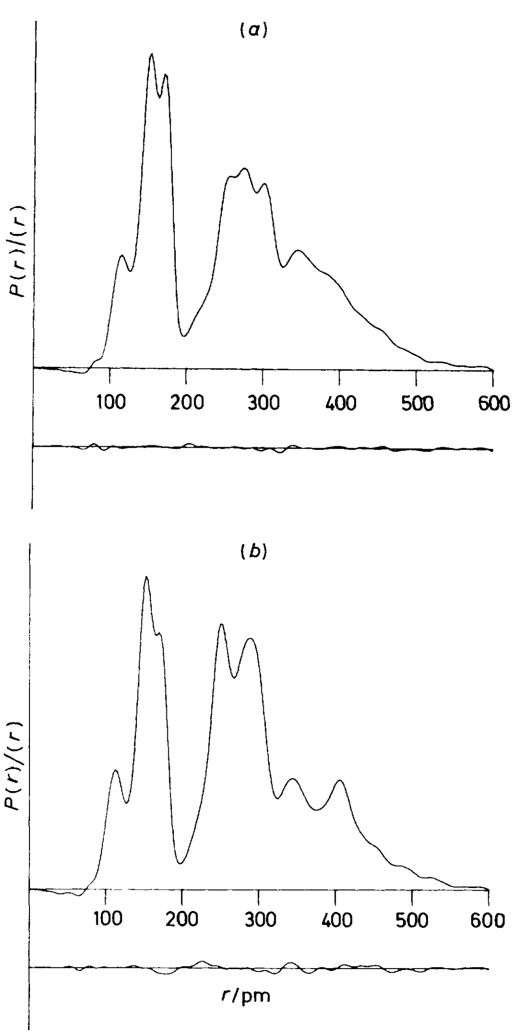

Figure 1. Observed and final weighted difference radial distribution curves, $P(r)/r$, for (*a*) $\text{NPr}^i(\text{SiH}_3)_2$ and (*b*) $\text{NBu}^t(\text{SiH}_3)_2$. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.00002\ s^2)/(Z_{\text{Si}} - f_{\text{Si}})(Z_{\text{N}} - f_{\text{N}})$

local C_2 symmetry, and this constraint was in fact applied in the final refinements for both compounds.

The conformation of the butyl group in $\text{NBu}^t(\text{SiH}_3)_2$ was defined by a twist angle about the C–N bond, relative to the position in which one C–C bond lay in the plane perpendicular to the SiNSi plane. The torsion angles of the three CH_3 groups were constrained to give the butyl group local C_3 symmetry overall.

With the geometries of the molecules constrained in these ways, they were described by the parameters listed in Table 4.

Refinement of $\text{NPr}^i(\text{SiH}_3)_2$ *structure.* The radial distribution curve for $\text{NPr}^i(\text{SiH}_3)_2$ [Figure 1(*a*)] shows three peaks in the region associated with bonded distances, with distinct peaks for the C–H and Si–N distances, but with those for Si–H, C–N, and C–C overlapping. Nevertheless all five bonded distances could be refined, although there was some correlation between the Si–H and C–N distances (Table 5), and three vibrational parameters were also refined. Vibrational parameters and details of any constraints used in the refinements are given in Table 6, with the list of interatomic distances.

Atoms separated by two bonds gave rise to a broad peak in the radial distribution curve, with three maxima at *ca.* 250, 280, and 300 pm. The first of these includes contributions from C(C)N and C(C)C atom pairs, and consequently the CCC and CCN angles are strongly correlated, and have correspondingly large estimated standard deviations (e.s.d.s). The central peak arises from the Si(N)C atom pairs. These two distances do not have to be identical, because the overall conformation adopted by the molecule is such that one Si–N bond eclipsed the unique C–H bond of the isopropyl group, while the other lay *anti* with respect to this C–H bond. The Si_2N wag parameter was therefore allowed to refine, and with the final value of the 2.7° the Si(N)C distances were 274 and 281 pm. The third peak of this group represented the Si(N)Si atom pair alone, and so the SiNSi angle was refined without difficulty.

The long Si ··· C distances depend on the C–N twist angle, which refined easily. Of the four distances only the one at 345 pm gave a distinct maximum in the radial distribution curve, but two vibrational parameters could be refined for this set of distances. Other long-range distances depend on the Si–N,

Table 6. Interatomic distances (r_a/pm) and amplitudes of vibration (u/pm)

	$NPr^i(SiH_3)_2$		$NBu^t(SiH_3)_2$	
	Distance	Amplitude	Distance	Amplitude
r_1(Si–N)	172.7(1)	4.7(3)	173.5(1)	5.0(3)
r_2(C–N)	148.7(5)	4.1(4)	147.9(8)	4.6(5)
r_3(C–C)	155.0(6)		154.6(4)	
r_4(Si–H)	147.1(6)	8.2(tied to u_2)	150.1(8)	9.2(tied to u_2)
r_5(C–H)	113.6(3)	7.4(5)	111.9(4)	7.6(4)
r_6[Si(N)Si]	301.6(2)	7.7(3)	298.0(5)	7.6(6)
r_7[Si(N)C]	273.6(7)	7.9(7)	279.7(5)	7.7(5)
r_8[Si(N)C]	281.3(7)			
r_9[Si(NC)C]	317.5(12)	11.3(14)	297.5(14)	15.1(tied to u_6)
r_{10}[Si(NC)C]	344.6(12)			
r_{11}[Si(NC)C]	369.5(17)	16.8(16)	355.3(10)	23.3(22)
r_{12}[Si(NC)C]	394.3(16)			
r_{13}[Si(NC)C]			404.9(6)	11.0(8)
r_{14}[Si(NC)C]				
r_{15}[N(C)C]	250.9(12)	7.5(5)	246.6(8)	7.2(8)
r_{16}[C(C)C]	250.2(27)		253.0(12)	

Other Si ··· H, N ··· H, C ··· H, and H ··· H distances were included in the refinements, but are not listed here. Errors, quoted in parentheses, are estimated standard deviations obtained in the least-squares refinements, increased to allow for systematic errors.

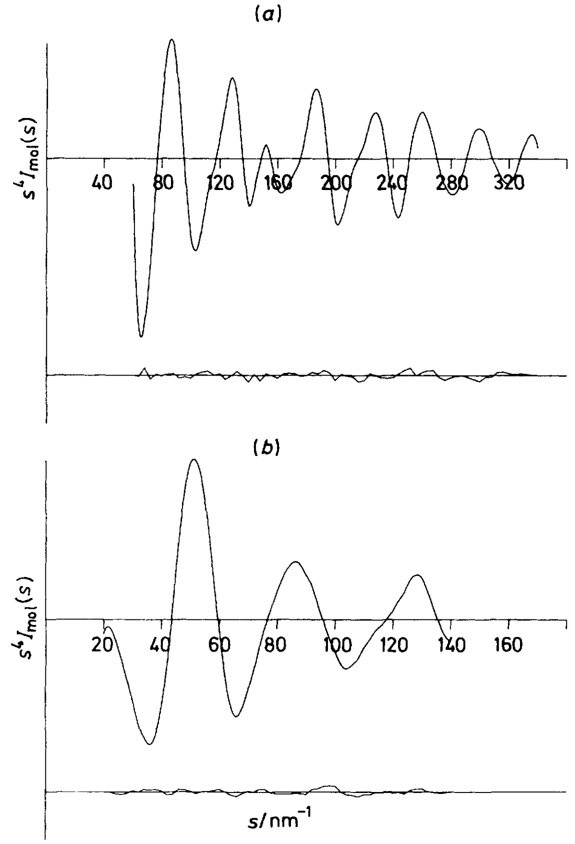

Figure 2. Observed and final weighted difference molecular scattering intensity curves for $NPr^i(SiH_3)_2$, recorded at camera distances of (*a*) 128 and (*b*) 286 mm

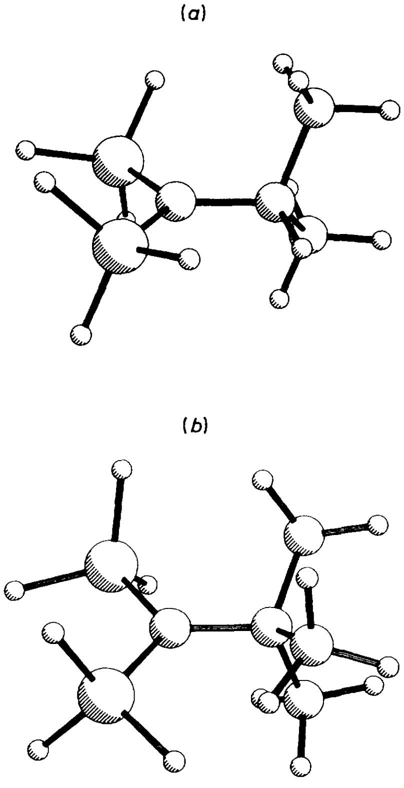

Figure 3. Perspective views of (*a*) $NPr^i(SiH_3)_2$ and (*b*) $NBu^t(SiH_3)_2$

C–N, and C–C twist angles, which were varied systematically over wide ranges to find favourable values before being refined. The standard deviations for the C–C and Si–N twist angles were then very large, so they were fixed in the final refinement, for which R_G was 0.07. The final geometrical parameters are listed in Table 4, interatomic distances and vibrational parameters in Table 6, and the least-squares correlation matrix in Table 5(*a*). The molecular scattering intensities are shown in Figure 2, and a perspective view of the molecule in Figure 3(*a*).

Refinement of $NBu^t(SiH_3)_2$ *structure.* The radial distribution curve for $NBu^t(SiH_3)_2$ [Figure 1(*b*)] is very similar to that for the isopropyl compound in the region below 200 pm. Again there were problems due to correlation between the Si–H and C–N bond lengths. With the Si–H distance fixed at 148.5 pm, the C–N distance refined to 148.7(9) pm. When the Si–H distance was freed, it refined to 150.1(8) pm, and the C–N distance

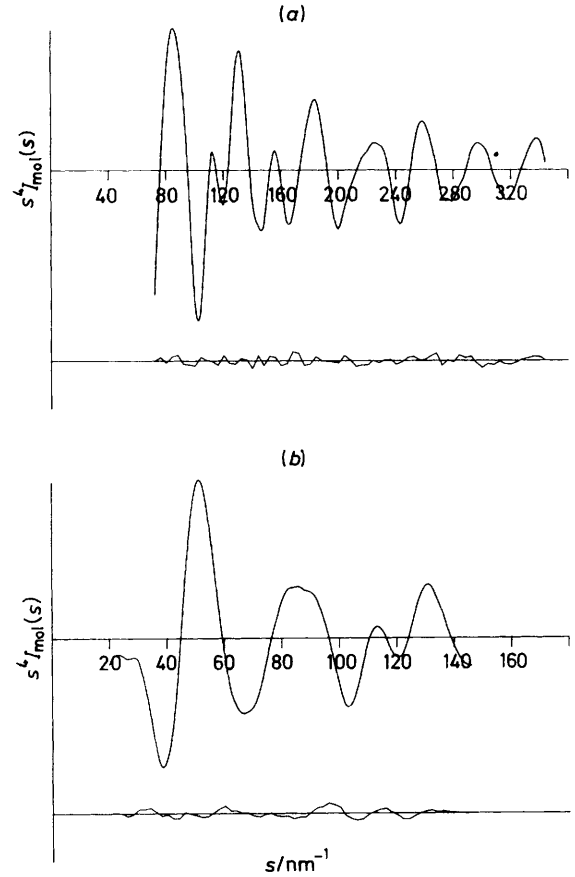

Figure 4. Observed and final weighted difference molecular scattering intensity curves for $NBu^t(SiH_3)_2$, recorded at camera distances of (*a*) 128 and (*b*) 286 mm

dropped to 147.9(8) pm. It is the results for the latter refinement which are quoted in Tables 4—6, and the *R* factor ratio test[12] indicates that they are significant at the 99% level.

Distances between pairs of atoms separated by two bonds again give a broad peak between 250 and 300 pm, but this time with just two maxima. The NCC angle determines the N(C)C and C(C)C distances, both of which are near 250 pm, and so this angle refined easily. The Si(N)C, Si(N)Si, and two long Si(NC)C distances all contribute to the maximum near 295 pm, and these distances define the SiNSi and SiNC angles, and also confirm the planarity of the $NCSi_2$ skeleton. The other long Si(NC)C distances give rise to peaks at 355 and 405 pm, and these help to define the C–N twist angle, which refined without difficulty. However, the Si–N and C–C twist angles were not well determined. Their values were varied over wide ranges to find the optimum values, and they were then refined.

The geometrical parameters, interatomic distances, and least-squares correlation matrix obtained in the final refinements, for which R_G was 0.09, are listed in Tables 4, 6, and 5 respectively. Molecular scattering intensities are shown in Figure 4, and Figure 3(*b*) is a perspective drawing of the molecule.

Discussion

Important geometrical parameters for the series of disilylamines, $NR(SiH_3)_2$ (R = H, Me, Et, Pr^i or Bu^t), are presented in Table 7. There is a striking reduction in the SiNSi angle as the bulk of the alkyl group is increased. The change from 125.2° in the methyl compound to 123.0° in the ethyl derivative occurs despite the fact that the C–C bond in the latter compound lies almost perpendicular to the plane of the other heavy atoms. The ethyl group does not lead to non-planarity at nitrogen, but to movement of the silyl groups towards each other. This movement is continued in the isopropyl amine, but here the conformation is such that the SiNC angles are not equal. The distortion can be regarded as a displacement of the N–C bond away from the more crowded silicon atom and towards the less crowded one. One SiNC angle is then slightly smaller than the angles in $NMe(SiH_3)_2$, while the other one is a little larger than those in the butylamine, in which the SiNSi angle is reduced below 120° for the first time, to 118.4°. The effect of adding more bulky substituents to the silicon atoms is the opposite of that observed here. In $NH(SiMe_3)_2$[13] and $NMe(SiMe_3)_2$[3] the SiNSi angles are increased, to 131.3(15) and 129.4(6)° respectively.

Table 7. Geometrical parameters (r_a) for disilylamines, $NR(SiH_3)_2$

	R				
	H	Me	Et	Pr^i	Bu^t
r(Si–N)/pm	172.5(3)	172.3(1)	172.6(1)	172.7(1)	173.5(1)
r(C–N)/pm		148.3(3)	146.1(5)	148.7(5)	147.9(8)
SiNSi/°	127.7(1)	125.2(2)	123.0(2)	121.6(2)	118.4(4)
SiNC/°		117.5(1)	118.5(1)	121.9(5) 116.5(5)	120.8(2)
Ref.	*	6	6	This work	This work

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The large changes in angles at nitrogen are accompanied by remarkably small variations in other parameters. Only in $NBu^t(SiH_3)_2$ is the Si–N bond lengthened significantly, by about 1 pm. In all the other disilylamines these distances are within 0.2 pm of 172.5 pm. However, even a methyl group on nitrogen lengthens the Si–N bonds by about this amount in the bis(trimethylsilyl)amines,[3,13] and we may therefore expect $NBu^t(SiMe_3)_2$ to show substantial effects of steric strain.

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