910. *Hydrogen Bond Formation with Silylamines.*

By S. W. Jarvie and D. Lewis.

The electron-donor ability of a number of dimethylsilylamines has been measured by a calorimetric method. The hydrogen-bonding capacity of the NH group in several different types of substituted silylamines has been determined from the solvent shifts, in the infrared region, of the N–H stretching mode.

It has been shown[1] that if chloroform is used as a reference acid alkylsilylamines are generally less basic than alkylamines, and under these conditions steric factors have a considerable influence on the base strength. The silylamines examined in the previous study were mainly trialkylsilyl derivatives. To elucidate further the influence of steric effects on the basicity of the silylamines we have synthesised a series of the less hindered dimethylsilylamines. The observed heats of mixing with chloroform are given in Table 1.

Table 1.

Heats of mixing (*M*) with chloroform (in cal. per mole of solution) at 17°.

$(SiHMe_2)_2NH$	70	$(SiMe_3)_2NH$	28 *	$SiMe_3{\cdot}NHPr^i$	174 *
$SiHMe_2{\cdot}NHEt$	438	$SiMe_3{\cdot}NHMe$	355 *	$SiMe_3{\cdot}NHBu^t$	98 *
$SiHMe_2{\cdot}NHPr^i$	199	$SiMe_3{\cdot}NHEt$	315 *	$NHPr^i_2$	935 †
$SiHMe_2{\cdot}NHBu^t$	132				

* Ref. 1. † Ref. 4 (temp. unstated).

The results for the trimethylsilyl series and di-isopropylamine are included for comparison. From these results it is apparent that the substitution of silicon for carbon has a considerable base-weakening effect. The simplest explanation would be that this is due to an electronic factor, but it may not be justifiable to assume that steric effects are completely absent, since such large differences in bond angles have been observed for the

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[1] Jarvie and Lewis, *J.*, 1963, 1073.

silyl[2] and carbon amines,[3] and we have noted differences in the steric behaviour in the two series within our own results. In both the trimethylsilyl- and the dimethylsilyl-amines there is a large decrease in base strength in passing from the *N*-ethyl to the *N*-isopropyl compound, and it seems likely that this is due to a steric factor. In the case of carbon amines no similar effect is observed; di-isopropylamine is a slightly stronger base than diethylamine,[4] and the increase in base strength is what would be expected from electronic effects.

In order to evaluate further the relative importance of steric and electronic factors, the acidities of the silylamines were determined by Cutmore and Hallam's method.[5]

It has been suggested[6] that the solvent shift observed in the infrared region for the X–H stretching frequency is due to solute–solvent dipolar association, and it was found that the slopes (S) of the straight lines obtained when the relative shifts of the frequencies were plotted against the corresponding shifts of some standard absorption band, for example, ν(N–H) pyrrole, paralleled the polarity of the X–H bond as measured by the pK_a value of the molecule. Since the pK_a value is dependent on the nature of the solvent it has been proposed by Hallam that the S value which is independent of any particular solvent provides a better measure of intrinsic acidity. Table 2a gives the N–H stretching frequencies of the silylamines in hexane solution, and Table 2b lists the shifts, $\Delta\nu$, of the N–H frequencies in various solvents; there is the relation

$$\Delta\nu/\nu = [\nu(\text{hexane}) - \nu(\text{solvent})]/\nu(\text{hexane}).$$

The vapour frequencies were not determined and the hexane frequency was taken as the reference point; this procedure does not affect the S values.

Table **3** gives the S values calculated for the silylamines, and the S values of some alkyl- and aryl-amines for comparison.

The acidities of the silylamines follow the type of pattern which one would predict from the previous studies on the silanols,[7] but several interesting points emerge. Increasing alkyl substitution at either the α-carbon or the α-silicon atom seems to have little effect on the acidity. The trimethylsilylamines and the dimethylsilylamines have almost identical S values. The accuracy of the S value is probably only about 5%, so minor differences in behaviour will not be observable by this method.

The proton-donating power of the disilazanes is similar to that of the aromatic amines. Kriegsmann[8] has shown spectroscopically that the Si–N bond order increases with increasing electronegativity of the substituent on the silicon atom and is higher in hexamethyldisilazane than in tetramethyldisilazane. One would, therefore, expect that hexamethyldisilazane would be rather more acidic than tetramethyldisilazane; in fact, the opposite is observed for both the disilazanes and the disiloxanes.[9]

Nuclear magnetic resonance studies[10] have shown that octamethylcyclotetrasiloxane is a weaker base than hexamethylcyclotrisiloxane, and it has been found by hydrogen-bonding methods that the linear methylpolysiloxanes are generally less basic than hexamethylcyclotrisiloxane. It has been inferred from these and other results that an increased bond angle at oxygen is accompanied by greater d_π–p_π bonding and a stronger Si–O bond.[11] In contrast, the S values show hexamethylcyclotrisilazane to be a stronger acid than

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[2] Kriegsmann, *Z. Elektrochem.*, 1957, **61**, 1088; Roper and Wilkins, *Trans. Faraday Soc.*, 1962, **58**, 1686; Yokoi and Yamasaki, *J. Amer. Chem. Soc.*, 1953, **75**, 4139.

[3] Sutton *et al.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, London, 1958.

[4] Tamres, Searles, Leighly, and Mohrman, *J. Amer. Chem. Soc.*, 1954, **76**, 3983.

[5] Cutmore and Hallam, *Trans. Faraday Soc.*, 1962, **58**, 40.

[6] Bellamy, Hallam, and Williams, *Trans. Faraday Soc.*, 1958, **54**, 1120.

[7] West and Baney, *J. Amer. Chem. Soc.*, 1959, **81**, 6145.

[8] Kriegsmann, *Z. anorg. Chem.*, 1961, **310**, 320.

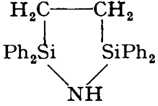
[9] West, Whatley, and Lake, *J. Amer. Chem. Soc.*, 1961, **83**, 763.

[10] Holzman, Lauterbur, Anderson, and Koth, *J. Chem. Phys.*, 1956, **25**, 172.

[11] Craig and Paddock, *J.*, 1962, 4118.

TABLE 2a.

N–H Frequencies (cm.$^{-1}$) of some silylamines in hexane solution.

$(SiPh_3)_2NH$	3370 *	$(SiMe_3)_2NH$	3381	$SiHMe_2{\cdot}NHPr^i$	3403
$[SiPh_2{\cdot}NH]_3$	3398 *	$[SiMe_2{\cdot}NH]_4$	3392	$SiHMe_2{\cdot}NHBu^t$	3392
	3436	$SiPh_3{\cdot}NHPr^i$	3397	$SiMe_3{\cdot}NHMe$	3427
		$SiPh_2(NHPh)_2$	3402 *	$SiMe_3{\cdot}NHEt$	3412
		$SiHMe_2{\cdot}NHEt$	3414	$SiMe_3{\cdot}NHBu^t$	3390
$(SiHMe_2)_2NH$	3390				
$[SiMe_2{\cdot}NH]_3$	3409				

* ν_{N-H} (hexane) estimated; a value was chosen so as to give a plot of relative shifts of the base against those of pyrrole, which is a straight line passing through the origin.

TABLE 2b.

Frequency shifts (cm.$^{-1}$) of some silylamines in various solvents (THF = tetrahydrofuran).

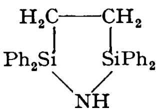
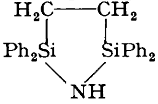
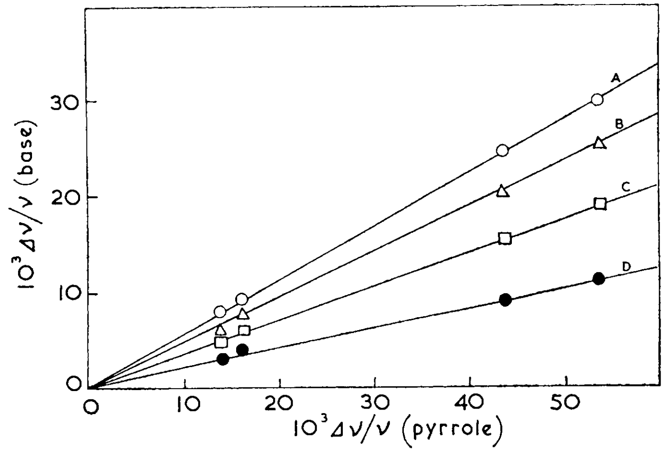
Compound		CCl_4	$CHCl_3$	C_6H_6	Anisole	Dioxan	$Bu^n{}_2O$	THF
$(SiPh_3)_2NH$	$\Delta\nu$	—	18	25	—	93	—	116
	$10^3\Delta\nu/\nu$	—	5·3	7·4	—	27·6	—	34·4
$[SiPh_2{\cdot}NH]_3$	$\Delta\nu$	—	10	25	34	93	—	117
	$10^3\Delta\nu/\nu$	—	2·9	7·3	10·0	27·4	—	34·4
	$\Delta\nu$	3	6	28	32	84	—	103
	$10^3\Delta\nu/\nu$	0·9	1·8	8·2	9·3	24·4	—	29·9
$(SiHMe_2)_2NH$	$\Delta\nu$	2	4	19	27	67	—	87
	$10^3\Delta\nu/\nu$	0·6	1·2	5·6	8·0	19·8	—	25·6
$[SiMe_2{\cdot}NH]_3$	$\Delta\nu$	2	3	17	25	60	—	74
	$10^3\Delta\nu/\nu$	0·6	0·9	5·0	7·3	17·6	—	21·7
$(SiMe_3)_2NH$	$\Delta\nu$	3	5	15	22	57	64	74
	$10^3\Delta\nu/\nu$	0·9	1·5	4·5	6·4	16·9	18·9	21·9
$[SiMe_2{\cdot}NH]_4$	$\Delta\nu$	1	3	14	21	53	—	65
	$10^3\Delta\nu/\nu$	0·3	0·9	4·1	6·2	15·6	—	19·1
$SiPh_3{\cdot}NHPr^i$	$\Delta\nu$	0	0	9	11	39	37	51
	$10^3\Delta\nu/\nu$	0	0	2·6	3·2	11·5	10·9	15·0
$SiPh_2(NHPh)_2$	$\Delta\nu$	—	5	21	38	75	—	93
	$10^3\Delta\nu/\nu$	—	1·5	6·2	11·2	22·1	—	27·3
$SiHMe_2{\cdot}NHEt$	$\Delta\nu$	1	—	12	16	32	32	36
	$10^3\Delta\nu/\nu$	0·3	—	3·5	4·7	9·4	9·4	10·5
$SiHMe_2{\cdot}NHPr^i$	$\Delta\nu$	2	—	11	16	32	30	38
	$10^3\Delta\nu/\nu$	0·6	—	3·2	4·7	9·4	8·8	11·2
$SiHMe_2{\cdot}NHBu^t$	$\Delta\nu$	1	—	10	14	30	—	38
	$10^3\Delta\nu/\nu$	0·3	—	2·9	4·1	8·8	—	11·2
$SiMe_3{\cdot}NHMe$	$\Delta\nu$	3	—	12	15	31	—	37
	$10^3\Delta\nu/\nu$	0·9	—	3·5	4·4	9·0	—	10·8
$SiMe_3{\cdot}NHEt$	$\Delta\nu$	2	—	10	13	30	28	36
	$10^3\Delta\nu/\nu$	0·6	—	2·9	3·8	8·7	8·2	10·5
$SiMe_3{\cdot}NHBu^t$	$\Delta\nu$	2	4	10	14	31	28	38
	$10^3\Delta\nu/\nu$	0·6	1·2	2·9	4·1	9·1	8·2	11·2
Pyrrole [6]	$10^3\Delta\nu/\nu$	1·7	5·7	13·6	15·9	43·4	45·9	53·7

TABLE 3.

S Values for some silylamines.

$(SiPh_3)_2NH$	1·6	$(SiHMe_2)_2NH$	2·1	$SiMe_3{\cdot}NHMe$	4·8
$[SiPh_2{\cdot}NH]_3$	1·6	$[SiMe_2{\cdot}NH]_3$	2·5	$SiMe_3{\cdot}NHEt$	4·8
	1·8	$(SiMe_3)_2NH$	2·5	$SiMe_3{\cdot}NHBu^t$	4·8
		$[SiMe_2{\cdot}NH]_4$	2·8	$NHPh_2$ [6]	1·8
		$SiPh_3{\cdot}NHPr^i$	3·7	$NHPhMe$ [6]	2·45
		$SiHMe_2{\cdot}NHEt$	4·8	NH_2Ph [6]	4·0
		$SiHMe_2{\cdot}NHPr^i$	4·8	$C_6H_{11}{\cdot}NH_2$ [6]	6·0
$SiPh_2(NHPh)_2$	1·9	$SiHMe_2{\cdot}NHBu^t$	4·8	$Ph{\cdot}CH_2{\cdot}NH_2$ [6]	7·0

octamethylcyclotetrasilazane. There is spectroscopic evidence which indicates that the six-membered cyclic silazanes[12] are rather less strained than the corresponding cyclic siloxanes. It has been shown that ring strain has the effect of shifting the ν_{as} Si-O-Si stretching vibrations to higher wavelengths. For five-membered cyclic siloxanes[13] this band occurs at 910—925 cm.$^{-1}$, for six-membered cyclic siloxanes[14] at 1010—1020 cm.$^{-1}$, and for linear and higher cyclic siloxanes[15] above 1050 cm.$^{-1}$, whereas for six-membered cyclic silazanes[12,16] the ν_{as} Si-N-Si vibrations occur in the same region as for the linear silazanes.[2,8,17] Further reduction in ring size introduces strain into the cyclic silazanes, causing a decrease in the acidity of the NH group. We have found that for five-membered cyclic silazanes the ν_{as} Si-N-Si vibrations lie at 865—870 cm.$^{-1}$ and the *S* value for 1,1,3,3-tetraphenyl-2-aza-1,3-disilacyclopentane is smaller than for hexaphenylcyclotrisilazane. However, the difference in acidity is small and lies just outside the experimental error of the measurements.



Solvent shifts for (A) 1,1,3,3-tetraphenyl-2-aza-1,3-disilapentane, (B) 1,1,3,3-tetramethyldisilazane, (C) octamethylcyclotetrasilazane, and (D) *N*-t-butyldimethylsilylamine.

It has been observed for alcohols,[18] amines,[5,19] and thiophenols[20] that the proton-donating power of the molecule and the basicity have an inverse relation to one another, and it is generally assumed that acidity and basicity are complementary. However, when the acidity and the basicity of the same species are being measured this is not necessarily true. West and Baney[7] have shown that the silanols are more acidic than the corresponding alcohols, and this enhanced acidity is not offset by a similar decrease in basicity.

The increased acidity of the silylamines relative to the carbon amines can probably be accounted for by d_π-p_π bonding, causing withdrawal of the single lone pair from the nitrogen, and it seems likely that this effect also decreases the basicity. To determine whether the acidity and the basicity of the NH group in the silylamines are complementary, an attempt was made to measure the donor properties of the nitrogen lone pair in hexaphenyldisilazane and hexaphenylcyclotrisilazane by means of the phenolic indicator,

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[12] Kriegsmann, *Z. anorg. Chem.*, 1959, **298**, 223.
[13] Piccoli, Haberland, and Merker, *J. Amer. Chem. Soc.*, 1960, **82**, 1883.
[14] Young, Servais, Currie, and Hunter, *J. Amer. Chem. Soc.*, 1948, **70**, 3758.
[15] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958.
[16] George, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1953, **75**, 6308.
[17] Fessenden, *J. Org. Chem.*, 1960, **25**, 2191.
[18] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2490.
[19] Bhowmik and Basu, *Trans. Faraday Soc.*, 1962, **58**, 48.
[20] Davis and Hallam, personal communication.

Bromophenol Blue.[21] The silylamines are generally decomposed by hydroxy-compounds, but hexaphenyldisilazane [22] can be recrystallised from ethanol, and hexaphenylcyclotrisilazane [23] can be dissolved in moist acetone and precipitated unchanged by water. Although the proton on the nitrogen will make the silicon more susceptible to nucleophilic attack, it was thought that if both the indicator and the silylamine were sufficiently bulky the reaction might be very slow and that it might be possible to measure the basicity spectroscopically. The silylamines gave the yellow colour with Bromophenol Blue normally given by aromatic amines, but the solutions decomposed so rapidly that it was impossible to obtain consistent results.

EXPERIMENTAL

Materials.—1,1,3,3-Tetramethyldisilazane was prepared by addition of dimethylchlorosilane (94 g., 1 mole) to liquid ammonia (200 ml.). The excess of ammonia was evaporated off and the residue extracted with dry ether. Fractional distillation of the product obtained after removal of the ether gave the tetramethyldisilazane (15 g., 0·11 mole), b. p. 94° (Found: *Si*-H, 1·55; N, 10·8. Calc. for $C_4H_{15}NSi_2$: *Si*-H, 1·52; N, 10·7%).

N-Alkyldimethylsilylalkylamines were prepared similarly from dimethylchlorosilane and the appropriate aliphatic amine, where alkyl = *ethyl*, b. p. 74°, n_D^{20} 1·3898 (Found: *Si*-H, 0·95; N, 13·3. $C_4H_{13}NSi$ requires *Si*-H, 0·97; N, 13·6%), *isopropyl*, b. p. 87°, n_D^{20} 1·3943 (Found: *Si*-H, 0·86; N, 12·1. $C_5H_{15}NSi$ requires *Si*-H, 0·86; N, 12·0%), and *t-butyl*, b. p. 108°, n_D^{20} 1·3940 (Found: *Si*-H, 0·76; N, 10·8. $C_6H_{17}NSi$ requires *Si*-H, 0·78; N, 10·7%).

Preparation of 1,1,3,3-*Tetraphenyl*-2-*aza*-1,3-*disilacyclopentane.*—Bis(chlorodiphenylsilyl)-ethane (115 g., 0·25 mole) in ether (200 ml.) was added to liquid ammonia (200 ml.), the mixture was stirred for an hour, and, when the ammonia had evaporated, ether (200 ml.) was added and the ammonium chloride filtered off. On removal of the ether an oil was obtained which on treatment with light petroleum gave a white crystalline *product* (4 g., 0·01 mole), m. p. 150° (Found: C, 76·4; H, 6·2; N, 3·7; Si, 13·8%; *M*, 395. $C_{26}H_{25}NSi_2$ requires C, 76·5; H, 6·1; N, 3·5; Si, 13·8%; *M*, 407).

The remainder of the amines used in this study were prepared by known methods.[24] The physical and analytical data for these materials are: Methyl-, b. p. 71°, n_D^{20} 1·3899 (Found: N, 13·6. Calc. for $C_4H_{13}NSi$: N, 13·6%), ethyl-, b. p. 90—91°, n_D^{20} 1·3930 (Found: N, 12·0. Calc. for $C_5H_{15}NSi$: N, 12·0%), and t-butyl-trimethylsilylamine, b. p. 121—123°, n_D^{20} 1·4055 (Found: N, 9·5. Calc. for $C_7H_{19}NSi$: N, 9·6%). Hexamethyldisilazane, b. p. 126°, n_D^{20} 1·4070 (Found: N, 8·6. Calc. for $C_6H_{19}NSi_2$: N, 8·7%). Hexamethylcyclotrisilazane, b. p. 188°, n_D^{20} 1·4439 (Found: N, 19·5. Calc. for $C_6H_{21}N_3Si_3$: N, 19·2%). Octamethylcyclotetrasilazane, m. p. 97° (Found: N, 18·9. Calc. for $C_8H_{28}N_4Si_4$: N, 19·2%): N-*isopropyltriphenylsilylamine*, m. p. 63° (Found: N, 4·5; Si, 8·9. $C_{21}H_{23}NSi$ requires N, 4·4; Si, 8·9%). Hexaphenyldisilazane, m. p. 175° (Found: N, 2·6. Calc. for $C_{36}H_{31}NSi_2$: N, 2·6%). Hexaphenylcyclotrisilazane, m. p. 213° (Found: N, 7·0. Calc. for $C_{36}H_{33}N_3Si_3$: N, 7·1%). Dianilinodiphenylsilane, m. p. 160° (Found: N, 7·3; Si, 7·6. Calc. for $C_{24}H_{22}N_2Si$: N, 7·6; Si, 7·6%).

The solvents were dried and distilled.

Calorimetry.—The apparatus and method used were identical to those previously described.[1]

Spectra.—The infrared spectra were determined by using a Unicam S.P. 100 double-beam grating spectrometer. Cells with path lengths of 0·5 and 1 mm. were used, absorptions due to solvents being eliminated by use of a variable-path compensating cell in the reference beam. The concentrations of the solutions were approximately 0·07M. Frequency values were measured to within ±2 cm.$^{-1}$ for the sharper bands. The machine was calibrated by using ammonia gas.

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[21] Bell and Bayles, *J.*, 1952, 1518.

[22] Reynolds, Bigelow, and Kraus, *J. Amer. Chem. Soc.*, 1929, **51**, 3071.

[23] Larsson and Bjellrup, *J. Amer. Chem. Soc.*, 1953, **75**, 993.

[24] Fessenden and Fessenden, *Chem. Rev.*, 1961, **61**, 361.