Direct EPR Evidence for Si–N dπ–pπ Bonding in Silylamine Radical Cations

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A series of amine radical cations with α-silyl substituents has been studied by EPR spectroscopy, following γ-radiolysis of dilute solutions of the parent amines in $CFCl_3$ at 77 K. It is clear that the nitrogen centred singly occupied molecular orbitals (SOMOs) are delocalised and extend appreciably onto the silyl groups, as shown by a fall in the magnitude of the anisotropic ^{14}N couplings from those found in alkylamine radical cations, and thus the concept of Si–N dπ–pπ bonding in silylamines is strongly supported. The results contrast with prior conclusions for the isoelectronic alkyl radicals *i.e.* the extent of spin delocalisation onto the silyl group is negligible.

Additionally, there is considerable variation in the effective McConnell Q_H-values throughout the series, and we propose that this is due to variations in the electron charge on the nitrogen atom centres.

The radical cation of tetrakis(trimethylsilyl)hydrazine, $(Me_3Si)_2N–N(SiMe_3)_2^{\cdot+}$, was found to adopt a twisted geometry with an angle between the two ^{14}N tensors [and hence the $N(2p_z)$ orbitals] of $<24°$. This is essentially in accord with the conclusions drawn from a liquid phase study of this cation by Bock *et al.*, but the twist angle is smaller than their estimate of 45°. This indicates that the N–N torsional potential may be quite shallow so that the cation is undergoing torsional averaging at the higher temperature used in the liquid state study.

The existence of partial π-bonding between a silicon atom and nitrogen, oxygen or fluorine substituents has been inferred from the well known observation that the bonds between silicon and these elements are short compared with the sums of the covalent radii.[1] Additionally, the bond angles Si–O–Si and Si–N–Si in siloxanes[1] and silylamines[2] are large compared with their organic counterparts, so that compounds such as $(H_3Si)_3N$ are actually planar at the nitrogen centre.[2] The nature of the partial bonding responsible for these effects has most often been attributed to delocalisation of lone-pair electron density into vacant silicon d-orbitals, and more recently to negative hyperconjugation involving Si–C σ*-orbitals.[3]

Conversely, it has been proposed that delocalisation of the unpaired electron, *via* dπ–pπ overlap, onto the substituents X in the series of alkyl radicals RĊHX (where X is a group IV or V substituent) is relatively unimportant, on the basis of the near constancy of the α- and β-proton couplings that are observed.[4] Clearly, direct information regarding the central atom hyperfine coupling is desirable, and with this intent we undertook the present study of the Me_3Si-substituted isoelectronic amine radical cations, in the expectation that anisotropic ^{14}N couplings would be readily observed, and thus provide a direct measure of the spin density at the radical centres and hence the degree of delocalisation in these radicals.

Experimental

Most of the silyl-substituted amines were purchased from either Aldrich, Fluka or Lancaster and were used as supplied. Tris(trimethylsilyl)amine was synthesised from bis(trimethylsilyl)lithium and a threefold excess of chlorotrimethylsilane in diethyl ether solution; m.p. 68–70 °C, lit.,[5] 69–70 °C. A sample of tetrakis(trimethylsilyl)hydrazine was supplied by Dr. Brian Roberts (University College, London). Trichlorofluoromethane was obtained from Aldrich and was further purified by filtering twice through activated silica.

Dilute solutions of the substrates were prepared in trichlorofluoromethane and were frozen in liquid nitrogen to form small polycrystalline beads which were irradiated at 77 K to a dose of 1.5 Mrad † using a ^{60}Co source. The EPR spectra were recorded using a Bruker ER 200D spectrometer with the sample contained in a liquid nitrogen filled insert Dewar, supported in the microwave cavity of the spectrometer. Field calibrations were made with an NMR gaussmeter.

Sample annealing was performed either by decanting the liquid nitrogen coolant from the sample Dewar and allowing the sample to warm, while continuously monitoring the EPR spectrum, then re-cooling to 77 K when significant spectral changes were observed, or with a Bruker variable temperature device, when specific temperatures were required.

Results and Discussion

The hyperfine data for silylamine radical cations are shown in Table 1, some of which were presented in preliminary form at a recent conference.[6] Relevant literature results for amine radical cations are also included for comparison.
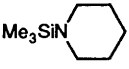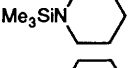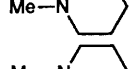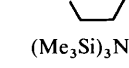
Alkylamine Radical Cations.—Simple amine radical cations have been studied in fluid acidic solutions[7] and in ionic crystal[8–11] or solid freon[12,13] matrices. The parent species, $NH_3^{\cdot+}$, was observed by Cole[8] in X-irradiated $NH_4^+ClO_4^-$, but was undergoing restricted rotation on the EPR timescale so that the anisotropic ^{14}N hyperfine tensor was partially averaged and thus a 'base' value for a species with unit spin density in the $N(2p_z)$ orbital is not provided. Therefore, we have used the standard parameters[14] along with data for alkylamine radical cations that were obtained mainly in non-polar polycrystalline matrices[12,13] and should thus yield the true values of the hyperfine tensors since the cations will not be significantly perturbed in these media.

Belevsky *et al.*[12] studied $Me_2NH^{\cdot+}$ in $CFCl_3$ at 77 K and were able to resolve the 4.3 G ‡ perpendicular coupling: thus the data in Table 1 for this radical are directly measured and are not subject to uncertainties in $A_\perp$. For nitrogen centred π-
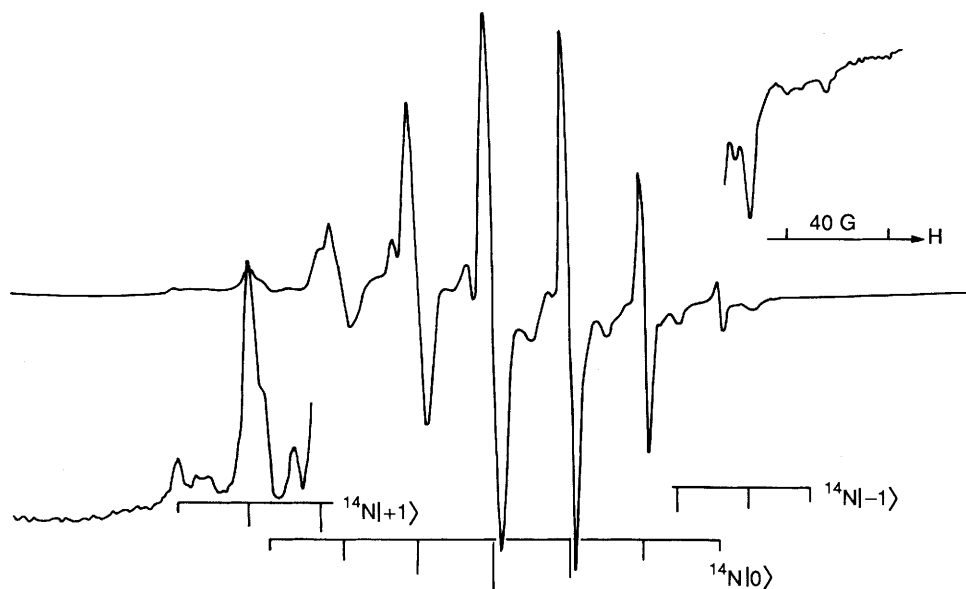
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† 1 rad = 0.01 Gy.

‡ 1 G = 10^{-4} T.

Table 1 Hyperfine coupling constants for amine radical cations

Radical	Coupling constants/G [a]				
	$A(^1H)$	$A_\parallel(^{14}N)$	$A_\perp(^{14}N)$ [b]	$A_{iso}(^{14}N)$	$2B$
MeNH$_2$$^{\cdot+}$ [c]	46 (3 H), 22.5 (2 H)	49	5.5	20	29.0
Me$_2$NH$^{\cdot+}$ [c]	34 (6 H), 36 (1 H)$_\parallel$, 19 (1 H)$_\perp$	49	4.3	19.3	29.7
Me$_3$N$^{\cdot+}$ [d]	28.2 (9 H)	47	0 ± 4	18.3	28.7
Me$_3$SiNMe$_2$$^{\cdot+}$ [e]	30 (6 H)	40	0 ± 4	16.0	24.0
(Me$_3$Si)$_2$NMe$^{\cdot+}$ [e]	34 (3 H)	37	0 ± 4	15.0	22.0
(Me$_3$Si)$_2$NH$^{\cdot+}$ [e]	26 (NH), 24 (NH)	36	0 ± 4	14.7	21.3
(Me$_2$SiH)$_2$NH$^{\cdot+}$ [e]	25 (NH)	35	0 ± 4	14.3	20.7
Me$_3$SiN⟨ring⟩$^{\cdot+}$ [e]	33 (2 H), ca. 5 (2 H)	38	0 ± 4	15.3	22.7
Me$_3$SiN⟨ring⟩$^{\cdot+}$ [e]	49 (2 H), 25 (2 H)	37	0 ± 4	15.0	22.0
Me—N⟨ring⟩$^{\cdot+}$ [c]	29 (3 H), 38 (2 H)	48	0 ± 4	18.7	29.3
Me—N⟨ring⟩$^{\cdot+}$ [c]	57 (2 H), 28 (3 H), 28 (2 H)	48	0 ± 4	18.7	29.3
(Me$_3$Si)$_3$N$^{\cdot+}$ [e]		35	0 ± 4	14.3	20.7
[(Me$_3$Si)$_2$N]$_2$$^{\cdot+}$ [e]		22(z), 5(x), 4(y)		10.3	11.7

[a] 1 G = 10⁻⁴ T. [b] Calculated using $A_\perp$ = +4 G, see text. [c] Refs. 11 and 12. [d] Ref. 10. [e] This work.

Fig. 1 EPR spectrum recorded at 77 K and assigned to Me$_3$SiNMe$_2$$^{\cdot+}$ radical cations isolated in a solid CFCl$_3$ matrix

radicals, $A_\perp$ is sufficiently small that it is not usually measurable in the experimental spectrum (the perpendicular |±1⟩ features being obscured by the intense central |0⟩ component) but lies within the range 0 ± 4 G. The spectra measured in this study are no exception to this, so that the derived values of A_{iso} and the dipolar coupling $2B$ must both be assigned a statistical error of ±2.7 G. However, a simple calculation for a localised tri-substituted amine radical cation, using published isotropic and dipolar coupling parameters suggests a value of $A_\perp(^{14}N)$ = +3.0 G, which is close to that actually measured for the Me$_2$NH$^{\cdot+}$ radical cation;[12] for a similar radical, but delocalised so that ρN(2p) = 0.6 [i.e. the most delocalised species in this study: (Me$_3$Si)$_3$N$^{\cdot+}$] we estimate $A_\perp(^{14}N)$ = +2.1 G. Thus it is probably safest to use the upper error limit [13] of $A_\perp(^{14}N)$ = +4.0 G throughout the series.

On first impression, it is curious that the measured

anisotropic coupling $(2B)$ in the MeNH$_2$$^{\cdot+}$ radical cation is less than that for Me$_2$NH$^{\cdot+}$ [12] since the presence of the second methyl group is expected to reduce the N(2p$_z$) spin population from that in MeNH$_2$$^{\cdot+}$. In fact, the order of their isotropic couplings accords with this expectation, and so the smaller MeNH$_2$$^{\cdot+}$ radical cation is almost certainly librating and thus partially averaging the dipolar coupling to nitrogen, so that the apparent $A_\parallel(^{14}N)$ falls below its true value.

Our best estimate of the N(2p$_z$) spin populations in these species is thus: MeNH$_2$$^{\cdot+}$ = 0.95, Me$_2$NH$^{\cdot+}$ = 0.90 and Me$_3$N$^{\cdot+}$ = 0.87.

Me$_3$SiNMe$_2$ and (Me$_3$Si)$_2$NMe.—The spectra recorded from these compounds following γ-radiolysis as dilute solutions in CFCl$_3$ at 77 K are shown, respectively, in Figs. 1 and 2. Extraction of $A_\parallel(^{14}N)$ and proton hyperfine couplings (Table 1)
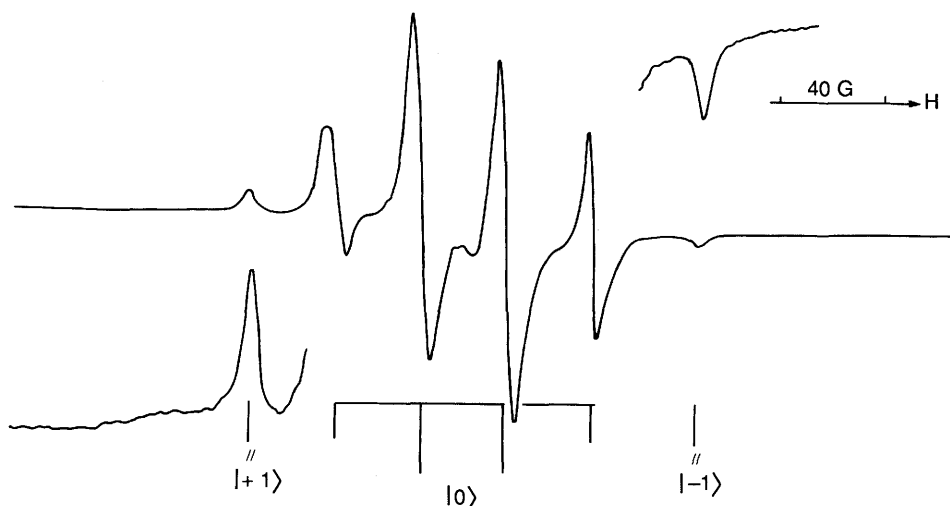
Fig. 2 EPR spectrum recorded at 77 K and assigned to $(Me_3Si)_2NMe^{•+}$ radical cations

is straightforward since these spectra are very well-resolved. It is apparent that each shows a pattern of central $|0\rangle$ features that broadens in the direction of low field: *i.e.* each feature arising from a state $+m_I$ is broader than that from the corresponding state $-m_I$, although the broadening increases with increasing m_I for both $(+)$ and $(-)$ series. This arises from the fact that $g_\perp > g_\|$ and the maximum value of the β-proton dipolar tensor (z) lies close to a perpendicular g-axis of the radical **I**. Thus
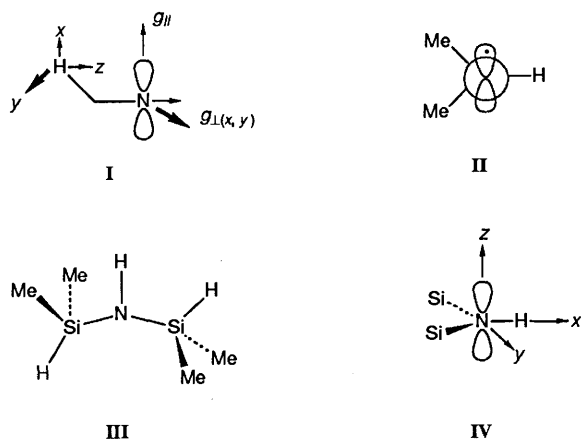
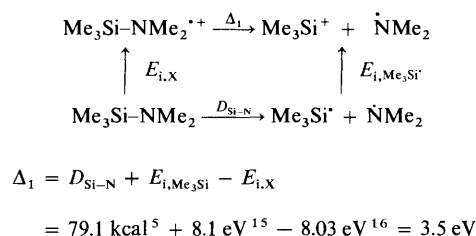$A_\| < A_\perp$ and since the widths of the solid state features depend on the $m_I(\perp) + m_I(\|)$ field variation, the asymmetric line-broadening is explained. In principle, the (x,y) hyperfine tensor components should be distinct, but the level of resolution does not permit comment on this. The rotation of the CH_3 groups partially averages the proton hyperfine anisotropy, but a residual positive component remains.

There is a clear fall in the magnitude of the dipolar couplings $(2B)$ from those reported for alkylamine radical cations, and thus the $2p_z$ spin populations in $Me_3SiNMe_2^{•+}$ and $(Me_3Si)_2-NMe^{•+}$ are 0.72 and 0.66, respectively. Therefore, in contrast with conclusions based on α- and β-proton couplings in alkyl radicals[4] of the type R_2CX (where X is a group IV or V substituent) that spin delocalisation by these substituents is relatively unimportant, we find substantial delocalisation by the silyl substituents in these isoelectronic silylamine radical cations. Thus the case is strong for Si–N dπ–pπ bonding in these radicals, and hence in the parent amines, since the singly occupied molecular orbital (SOMO) in a radical cation usually matches the highest occupied molecular orbital (HOMO) of the parent molecule in the absence of dramatic structural changes

occurring on ionisation. Clearly, a determination of the ^{13}C tensors in the alkyl radicals would prove worthwhile, since the dipolar ^{13}C couplings should provide a direct measure of the central atom $C(2p_z)$ populations. As we show later, α- and β-proton couplings are very sensitive to the precise nature of the substitution present, and thus for a given spin density can vary widely, according to the charge on the nitrogen atoms in these radicals.

In Fig. 1, there are weaker features present in addition to those from the primary radical cation, and these can be assigned to $Me_2N^•$ radicals. We suggest that these radicals arise from unimolecular fragmentation of the parent $Me_3SiNMe_2^{•+}$ radical cations. The thermochemical feasibility of this process can be assessed in terms of an energy cycle (Scheme 1). Since the

$$Me_3Si-NMe_2^{•+} \xrightarrow{\Delta_1} Me_3Si^+ + {}^•NMe_2$$

$$\uparrow E_{i,X} \qquad\qquad \uparrow E_{i,Me_3Si^•}$$

$$Me_3Si-NMe_2 \xrightarrow{D_{Si-N}} Me_3Si^• + {}^•NMe_2$$

$$\Delta_1 = D_{Si-N} + E_{i,Me_3Si} - E_{i,X}$$

$$= 79.1 \text{ kcal}[5] + 8.1 \text{ eV}[15] - 8.03 \text{ eV}[16] = 3.5 \text{ eV}$$

Scheme 1

difference between the ionisation potentials of $CFCl_3$[15] and Me_3SiNMe_2[16] amounts to *ca.* 2.9 eV, there may be sufficient energy available during the $CFCl_3^{•+}/Me_3SiNMe_2$ charge-transfer step to approach the dissociation threshold of the radical cation and so the observed small yield of $Me_2N^•$ is not unreasonable. The dissociation may also be assisted by bonding between the developing Me_3Si^+ fragment and a chlorine atom of the freon matrix. (Doubtless, other factors are also important: *e.g.* a similar calculation predicts that the acetone radical cation should be even more prone to fragmentation; however, in our study of this radical,[17] we were unable to detect the expected paramagnetic product of its decomposition, which is the methyl radical).

We did not detect features from similar neutral radicals in the spectra of any of the other silylamines under our conditions, suggesting either a considerably diminished yield of such species or simply that features from their expectedly narrower spectra are concealed by the much more intense features from the intact primary silylamine radical cations.

$(Me_3Si)_2NH, (Me_2SiH)_2NH$ *and* $(Me_3Si)_3N$.—The spectra
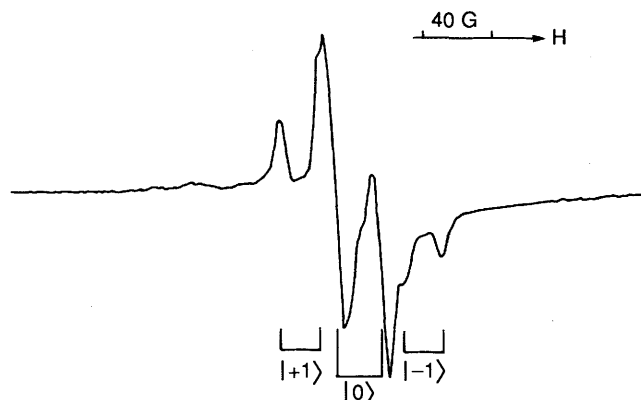
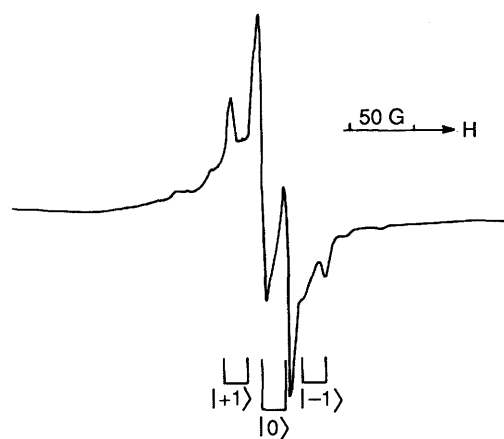Fig. 3 EPR spectrum assigned to $(Me_3Si)_2NH^{•+}$ radical cations at 77 K

Fig. 4 EPR spectrum assigned to $(Me_2SiH)_2NH^{•+}$ radical cations at 77 K

(a)

(b)

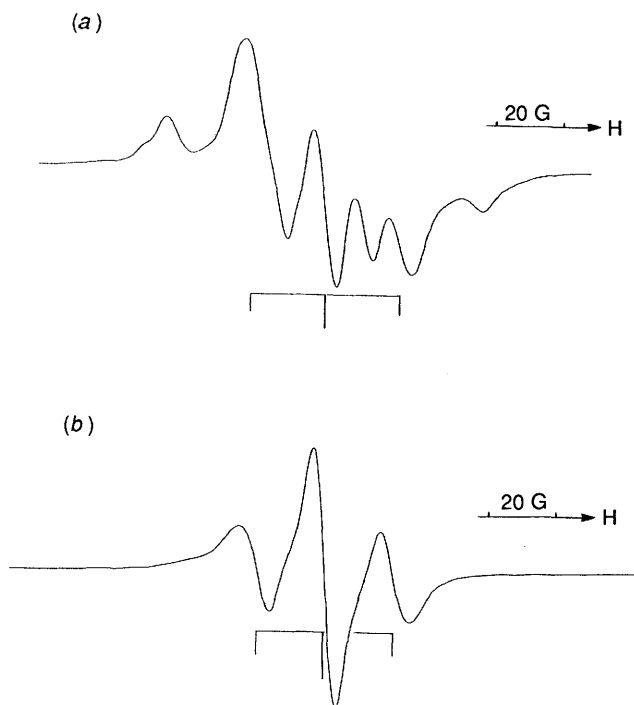Fig. 5 EPR spectrum recorded at 77 K: (a) following γ-irradiation of a 10% solution of $(Me_3Si)_2NH$ in $CFCl_3$, followed by annealing at 150 K, and assigned to a mixture of the parent $(Me_3Si)_2NH^{•+}$ radical cation and the radical $H_2CSiMe_2NHSiMe_3$, arising via reaction (2); (b) following γ-irradiation of pure $(Me_3Si)_2NH$, assigned to H_2CSiMe_2-$NHSiMe_3$ radicals

recorded from the first two compounds are shown in Figs. 3 and 4, and are assigned to the primary radical cations. They are of remarkably similar appearance, and yield equal $N(2p_z)$ spin populations of 0.63; therefore, these are highly delocalised species. It seems surprising that there is no resolved coupling to the β-Si–H protons in the spectrum (Fig. 4) of the $(Me_2SiH)_2NH^{•+}$ radical cation, but this must reflect an essentially fixed orientation of the silyl groups (II) so that the Si–H protons lie close to the nodal plane of the radical. This behaviour is in sharp contrast with results for other radicals: for instance, in the radical cation of dimethylsilylbenzene[18] $(Me_2SiHPh^{•+})$ the Si–H bond tends to adopt a perpendicular orientation with respect to the ring plane, and so it was concluded that the conformation was dictated by the electronic effect of hyperconjugation, involving the Si–H bonding electron pair, rather than that of a Si–C bond, this overriding steric control. Structure III actually maximises Si–C overlap with the $N(2p_z)$ orbital, but also corresponds to a steric minimum in that this orientation reduces the non-bonded interactions between the pairs of methyl groups in the overall C_s structure III. We conclude therefore that in this case it is the steric effect which dominates.

It is perhaps surprising that the α-N–H-proton couplings in these radicals are so nearly isotropic. We propose that this is due to librational motion within the x,y plane (IV), an effect that would average the A_x $(+B)$ and A_y $(-B)$ hyperfine anisotropy, the component along z remaining nearly isotropic: $A_z = 0$. The possibility that these cations are librating is worrying because motion in either the x,z or y,z planes would reduce the measured anisotropic ^{14}N coupling $(2B)$ from the true value and lead to the calculation of lower spin populations than actually exist; and, rather, we have interpreted the fall in $(2B)$ in terms of spin delocalisation onto the silyl substituents. The following argument, however, adds confidence to our interpretation and eliminates the presence of significant motion of the $A_z(^{14}N)$ tensor axis into either plane.

For libration in the x,z plane, the proton hyperfine tensor would be modulated (using the axis system defined in IV) such that A_x $(+B)$ and A_z $(=0)$ are averaged. Thus the A_z coupling would be greater than the observed isotropic value and there would still be a considerable difference between A_y and the averaging A_z/A_x component. Similar reasoning rules out motion in the y,z plane, since the averaging A_z/A_y component should differ appreciably from A_x. Thus the case for x,y motion appears strong, but it still seems odd that a cation of this size should be librating when the highly anisotropic α-proton tensor that was observed for the much smaller $Me_2NH^{•+}$ radical cation[12] shows it to be 'fixed' on the EPR timescale at 77 K.

Belevsky's study of $Me_2NH^{•+}$ in $CFCl_3$[12] showed that at high concentrations of Me_2NH, $Me_2N^{•}$ radicals were formed through the ion-molecule, reaction (1). Similarly, we hoped to

$$Me_2NH^{•+} + Me_2NH \longrightarrow Me_2NH_2^+ + Me_2N^{•} \quad (1)$$
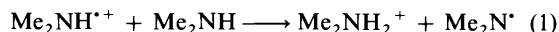
form the radical $(Me_3Si)_2N^{•}$ and therefore study much more concentrated solutions (up to ca. 15%) than normal. Unfortunately, while features were observed from a secondary radical, in addition to those from the primary radical cation [Fig. 5(a)], they could not be reasonably assigned to the desired species, but to the radical $\dot{C}H_2SiMe_2NHSiMe_3$. [The identical radical was also formed by γ-radiolysis of the pure compound: $A(2 H) = 20.0$ G, Fig. 5(b).] Thus the favoured ion–molecule reaction involves abstraction of a hydrogen atom from a CH_3–Si group rather than from the N–H group. This difference from reaction (1) may be partly the result of a purely statistical factor, but the α-silicon substituents should activate the C–H bonds towards H-atom abstraction. However, the nitrogen lone-pair in Me_2NH should also activate the adjacent C–H bonds
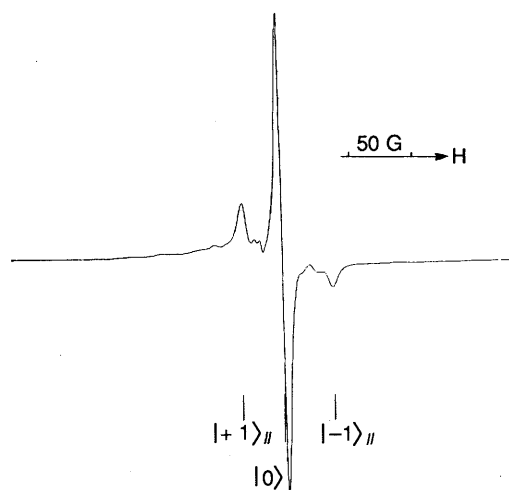
Fig. 6 EPR spectrum assigned to $(Me_3Si)_3N^{•+}$ radical cations at 77 K
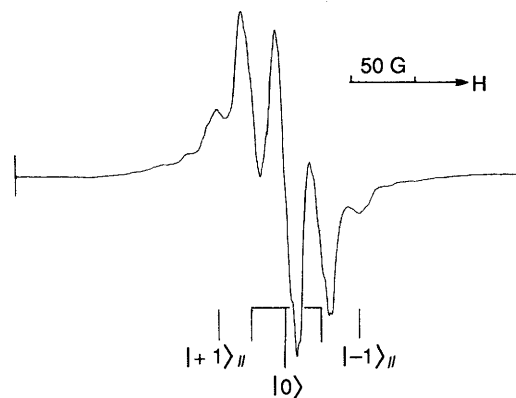

Fig. 7 EPR spectrum assigned to 1-trimethylsilylpiperidine radical cations at 77 K
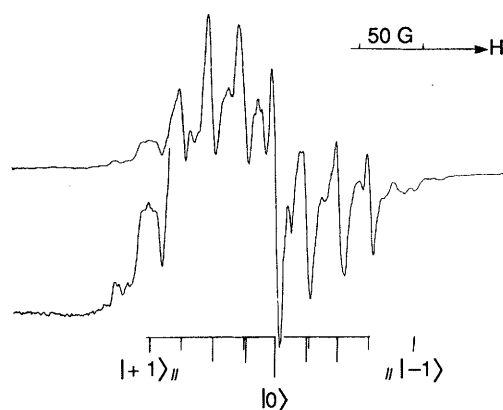

Fig. 8 EPR spectrum assigned to 1-trimethylsilylpyrrolidine radical cations at 77 K

towards homolytic cleavage by stabilisation of the resulting radical ($H_2\dot{C}$–$\ddot{N}HMe \longleftrightarrow H_2\bar{C}$–$\overset{+}{N}HMe$).

It is most probable that these reactions are actually of completely different character, i.e., reaction (1) involves proton transfer [reaction (1′)], while reaction (2) is a true H-atom abstraction. While (1′) may be the faster reaction for a normal amine, the more weakly basic character of $(Me_3Si)_2NH$ [19] results in a reduced rate for proton transfer, so that the H-transfer step, reaction (2), dominates.

The results for the $(Me_3Si)_3N^{•+}$ radical cation (spectrum shown in Fig. 6) are unexpected in that the $2B$ parameter shows that the introduction of the third silyl group reduces the $N(2p_z)$
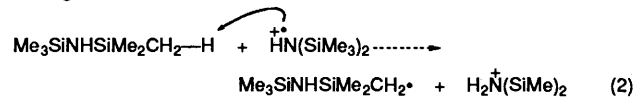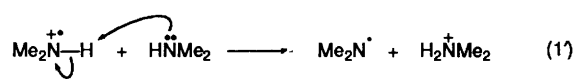
spin population by only a negligible amount (2%) from that in the disilylamine cations. Indeed, it is apparent that the relative spin delocalising effect of the silyl substituents is rapidly attenuated by their increasing number. Since spin delocalisation from the $N(2p_z)$ orbital onto the α-silyl substituents involves vacant silicon based orbitals, it amounts to depletion of π-electron density from the nitrogen atom. Accordingly, the positive charge on the nitrogen atom must increase with each substitution, thus lowering the $2p_z$ energy and decreasing the overlap with the higher lying silicon levels. Thus, following the pronounced effect of the first substituent, that of the second and third are consequently much less.

Cyclic Silylamine Radical Cations.—The radical cations of 1-trimethylsilylpiperidine and 1-trimethylsilylpyrrolidine were studied; the spectra recorded therefrom are shown in Figs. 7 and 8. In each case, there is delocalisation of the unpaired electron onto the silyl group, but the rings are seen to provide very similar orientations of the β-C–H bonds to those in the radical cations of their N-alkyl analogues (Table 1) as studied by Symons et al.[13] It is interesting, and noteworthy, that the conformations of the rings in five- (**V**) and six- (**VI**) membered
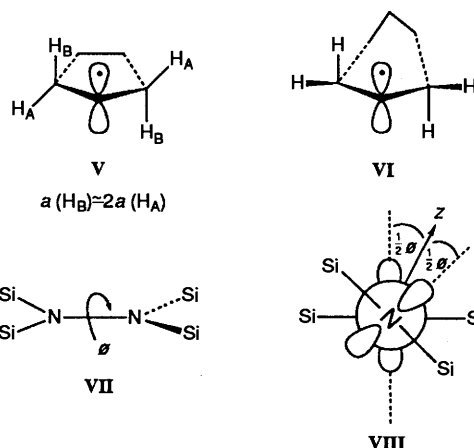
cyclic radicals are essentially preserved across a range of species,[12,20–25] despite the presence of differing elements and varying spin densities at the radical centres, and appear to be a function of steric requirements of the rings themselves, with electronic factors playing a relatively minor role.

$(Me_3Si)_2N$–$N(SiMe_3)_2$.—The EPR spectrum of this radical cation in the liquid phase has been studied by Bock et al.[26] As expected, there is extensive delocalisation of spin density onto the silyl groups via π-delocalisation and also via direct Si–N σ–π conjugation since the cation apparently adopts the twisted structure **VII** with planar Si_2N units and a twist angle θ of 45°. A spectrum of this cation in solid $CFCl_3$ at 77 K is shown in Fig. 9, from which the ^{14}N hyperfine components were extracted: $A_x = 5$, $A_y = 4$, $A_z = 22$ G. The magnitude of the parallel coupling A_z eliminates the assignment of a similar structure in the solid matrix to that present in fluid solution because it implies a dipolar coupling ($2B$) of 14.5 G, using Bock's isotropic value of 7.52 G. This leads to a 2p spin population on each nitrogen atom of 0.44, in contrast with the value (0.33)
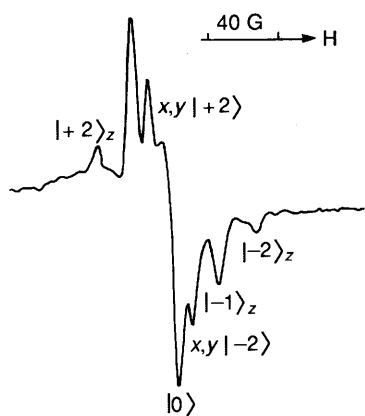
Fig. 9 EPR spectrum recorded at 77 K and assigned to $(Me_3Si)_2N-N(SiMe_3)_2^{•+}$ radical cations

Table 2 Q-Values calculated for amine radical cations

Radical	N(2p$_z$) Spin density	Q_{Me}^{H}	Q_{N-H}^{H}
MeNH$_2^{•+}$	0.95	48.4	23.7
Me$_2$NH$^{•+}$	0.896	37.9	27.5
Me$_3$N$^{•+}$	0.866	32.6	—
Me—N (six-membered ring) $^{•+}$	0.884	32.8	—
Me—N (five-membered ring) $^{•+}$	0.884	31.7	—
Me$_3$SiNMe$_2^{•+}$	0.724	41.4	—
(Me$_3$Si)$_2$NMe	0.664	51.2	—
(Me$_3$Si)$_2$NH$^{•+}$	0.642	—	38.4
(Me$_2$NH)$_2$NH$^{•+}$	0.624	—	40.1

obtained from the ratio of isotropic couplings in this and the $H_2N-NH_2^{•+}$ radical cation (11.5 G),[27] where $\rho 2p$ can be taken as *ca.* 0.5. However, this derivation of a nitrogen spin population from the $2B$ value only applies to the fully planar structure where both ^{14}N tensors are parallel, and actually represents a lower limit on the spin population, since twisting about the N–N bond introduces an angle θ between the z-axes **(VIII)** and thus reduces the measured maximum dipolar coupling (corresponding to the situation where the axis of the applied field z now bisects θ) below the true value for each tensor. For a 45° twist, the apparent parallel coupling (A_z') should be given by eqn. (3) at 16 G, and is much lower than the

$$A_z' = A_{iso} + \left\{ \frac{(3\cos^2 \frac{1}{2}\theta - 1)}{2} \cdot \rho 2p_z \cdot B_0 \right\} \qquad (3)$$

experimental value, which therefore suggests a more planar structure.

The experimental spectrum (Fig. 9) contains perpendicular $|\pm 2\rangle$ features, corresponding to the couplings given above, from which an isotropic coupling $A_{iso} = 10.3$ G along with a nitrogen 2p spin population of 0.352 may be derived. Thus the Si_2N units are slightly pyramidal, but not by more than *ca.* 0.5° (R–N–R, $\varphi = 119.5°$) according to the normal procedure[14] for estimating bond angles from s–p hybrid orbital populations through the appropriate Coulson equation,[28] after correcting the s-component[29] for the indirect contribution from σ–π spin polarisation.[30] There is an apparent discordance that exists between the measured π-spin population (0.352) and that calculated by taking Bock's[26] A_{iso} value for a tetrasilylhydrazine radical cation that is constrained towards a planar structure (8.68 G) and dividing by that for the hydrazine radical cation

(11.5 G).[27] This may be reconciled with a partially twisted structure for which eqn. (3) yields an angle θ of 24°. In this region, the $3\cos^2 \frac{1}{2}\theta - 1$ function is relatively insensitive to further reductions in θ and given the approximations used this value is merely an estimate. Nonetheless, for $\theta = 24°$, values of $A_x = 4.9$ G and $A_y = 4.1$ G (corresponding to the true perpendicular axis) are obtained, in remarkably good agreement with the experimental values. In any event, the more nearly planar arrangement of the cations at 77 K in the solid matrix than in fluid solution suggests that the N–N torsional potential has a relatively flat minimum on which the precise configuration of the cation can be partly influenced in one case by matrix effects and in the other by torsional averaging in fluid solution at the higher temperature employed: the flat potential allowing appreciable torsional amplitudes.

Annealing to 150 K merely resulted in the normal reversible shift of the parallel and perpendicular features associated with motional averaging of an anisotropic hyperfine tensor, and hyperfine parameters measured on re-cooling to 77 K after annealing were identical with those measured originally after both irradiation and measurement at 77 K.

Q-Values for Amine Radical Cations.—Table 2 shows the N(2p$_z$) spin populations for amine radical cations, derived from the anisotropic couplings (2B) given in Table 1, along with McConnell Q-values calculated for those cations bearing CH_3 and α-H substituents. It is immediately apparent that there is a trend in Q_{Me}^{H} values in the direction: $R_3N^{•+} < Me_2NH^{•+} < MeNH_2^{•+}$. In each case the substitution of an alkyl or a hydrogen atom substituent by a silyl group results in an increase in the Q_{Me}^{H} value. These effects may be explained in terms of changes in the electron charge associated with the nitrogen atom arising from the electronic influence of the various substituents: alkyl groups delocalise spin density by hyperconjugation, which increases the π-spin population on nitrogen and reduces the positive charge; silyl groups delocalise spin density into vacant orbitals and thus increase the positive charge density on nitrogen as its 2p$_z$ coefficient is decreased. The α-proton couplings also follow this trend, increasing with the excess positive charge on the nitrogen atoms.

These results are quite reassuring, in that they strongly support the widely held view that it is vacant silicon based orbitals that are responsible for the structural influence of silyl substituents on their compounds with oxygen, nitrogen or fluorine. The alternative of donation from filled silicon σ-Si–C orbitals would act in the same direction as the alkyl groups, contrary to observation. Any such σ-electronic effects are clearly of minor importance.

In view of this electron acceptor role of the silyl substituents, there exists the possibility that radicals of the type $R_nN(SiMe_3)_{3-n}^{•+}$ are captodatively stabilised.[31] This possibility can be checked with the eqn. (4), which is of similar form to

$$\rho_{\pi_x} = \prod_x (1 - \Delta\rho^x) \prod_{xy} (1 - \Delta\rho^{xy}) \qquad (4)$$

that used in our previous study of captodative interactions in muonated cyclohexadienyl radicals.[32]

From the experimental N(2p$_z$) spin populations ρ_x^{π} (Table 2) a set of equations was obtained, solution of which yielded values for both the first-order (substituent delocalisation) parameters ($\Delta\rho^x$) and the second-order (substituent interaction) parameters ($\Delta\rho^{xy}$). It is the latter that probe the pairwise interaction between the substituents and the π-system: if their mutual presence enhances their combined delocalisation effect will take a positive sign (synergetic); if their combined effect is attenuated, then $\Delta\rho^{xy}$ will be negative (antagonistic).

The parameters are: $\Delta\rho^{Me} = +0.060$, $\Delta\rho^{SiMe_3} = +0.249$,

$\Delta\rho^{Me-Me} = -0.014, \Delta\rho^{Si-Si} = -0.137, \Delta\rho^{Me-Me} = -0.045$. The very large negative parameter reflects the rapid attenuation of spin delocalising effect of silyl substituents as their number increases, referred to in an earlier section, and accords with the substantial increase in positive charge and lowering of the $2p_z$ orbital on nitrogen that is occasioned by silyl substitution. The antagonistic effect of polymethyl substitution, in contrast, arises from successive enhancements in the $N(2p_z)$ orbital energy which remove it increasingly from the lower-lying filled C–H levels.

A negative value for the $\Delta\rho^{Me-Si}$ parameter is rather unexpected, however, and shows that the silyl and methyl substituents are strongly antagonistic, in contrast with prediction for such a captodative pair with opposite electronic influences. An explanation for this is not clear at present.

Conclusions

The present results show quite definitely that there is significant $d\pi$–$p\pi$ bonding in silylamine radical cations, and by implication in the parent silylamines, in agreement with previous views.[2,16,33] It is clear that it is vacant silicon-based orbitals that are involved, because the interaction appears to increase the positive charge on the nitrogen atom; overlap between the nitrogen 2p orbitals and filled σ-Si–C orbitals would release electron density, and so decrease the positive charge on nitrogen. It is most likely that these vacant orbitals are d-orbitals, but the involvement of σ*-Si–C-orbitals[3] cannot be ruled out by the present results.

In view of the sensitivity of the proton couplings to charge variations at the radical centres in the amine radical cations, it seems possible that the same may be true of carbon radical centres in alkyl radicals. Thus the observed constant values of proton couplings in substituted alkyl radicals[4] may be partly artificial, with the reductions in these couplings expected by delocalisation being offset by increases in the effective Q-values as the positive charge is increased by the delocalisation into vacant substituent orbitals. A study of the ^{13}C labelled radicals would be worthwhile to obtain detailed and direct information regarding the spin densities at the radical centres.

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