

RADICAL IONS

XXVIII *. TRIS(TRIMETHYLSILYLMETHYL)AMINIUM, $\cdot^+N(CH_2Si(CH_3)_3)_3$: A STABLE FLUXIONAL AMINIUM RADICAL CATION

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Summary

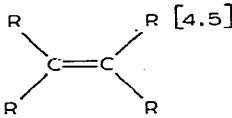
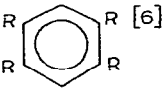
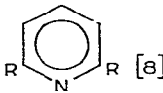
The first ionization potentials of 11 silylmethyl-substituted amines $R_{3-n}N-(CH_2Si(CH_3)_3)_n$ as determined by photoelectron spectroscopy range from 9.07 eV to 7.66 eV. The most easily ionized molecule, $N(CH_2Si(CH_3)_3)_3$, can also be oxidized with $AlCl_3$ in H_2CCl_2 solution to its aminium radical cation. The ESR spectra recorded between 180 K and 310 K display a strong temperature dependence due to rotations around the $>N-CH_2-$ bonds.

Introduction

Trimethylsilylmethyl substituents are powerful electron donors [2], which lower considerably most π and lone pair n_X ionization energies (e.g. (1)).

The reduced energy differences (1) between the ground states of the neutral molecules and the resulting radical cation states are best rationalized [9] in terms of a stabilizing delocalization of the positive charge [4,6]. Applying Koopmans theorem, $IE_n \approx -\epsilon_J^{SCF}$, and using perturbation arguments [5–11], the replacement of substituents (1) e.g. CH_3 by $CH_2Si(CH_3)_3$ destabilizes the highest occupied orbital both inductively ($Z_{eff}^{Si} < Z_{eff}^C$) and due to increased hyperconjugation ($\pi/\sigma_{CSi} > \pi/\sigma_{CH}$ or $n_X/\sigma_{CSi} > n_X/\sigma_{CC} > n_X/\sigma_{CH}$) [5–11]. Because only few examples of n_X/σ_{CSi} interactions have been investigated so

* For part XXVII see ref. 1a, also part LXXX of Photoelectron spectra and molecular properties, for part LXXIX see ref. 1a, and part CXIV of Chemistry of organosilicon compounds, for part CXIII see ref. 1b.

$IE_1(\pi):$	$R-C\equiv C-R$ [2b, 3]	 [4.5]	 [6]
$R = H$	11.40 eV	10.51 eV	9.24 eV
CH_3	9.61	8.31	8.05
$CH_2Si(CH_3)_3$	8.85	7.15	7.10
	0.76 eV	1.16 eV	0.95 eV
			(1)
$IE_1(n_X)$	$R-S-R$ [7]		 [8]
$R = H$	10.43 eV		
CH_3	8.67	$R = H$	9.6
CH_2CH_3	8.44	CH_3	9.3
$CH_2Si(CH_3)_3$	8.04	$Si(CH_3)_3$	8.5
	0.23 eV		0.3 eV
	0.40 eV		0.8 eV

far [7,10], we wish to report PES and ESR data for silylmethyl-substituted amines and their aminium radical cations, which were generated by one-electron ionization in the gas phase and, in case of the title compound, also by one-electron oxidation in solution.

Experimental

Trimethylsilylmethyl-substituted amines (Table 1) prepared according to literature procedures were: tris(trimethylsilylmethyl)amine (I) [12], *N,N*-bis(trimethylsilylmethyl)ethylamine (II) [13], *N,N*-diethyl(trimethylsilylmethyl)amine (V) [13], *N*-(trimethylsilylmethyl)piperidine (VI) [14], *N,N*-dimethyl(trimethylsilylmethyl)amine (VII) [15], bis(trimethylsilylmethyl)amine (VIII) [15], *N*-ethyl(trimethylsilylmethyl)amine (IX) [13], *N*-methyl(trimethylsilylmethyl)amine (X) [12], and trimethylsilylmethylamine (XI) [16].

N,N-Bis(trimethylsilylmethyl)methylamine (III) was isolated as a by-product from the 2 : 1 reaction mixture of chloromethylsilane and dimethylamine after 4 h at 410 K in an autoclave. After work-up distillation gave 46% of X and 26% of III (b.p. 333–343 K/18 mmHg) identified by NMR (C_6D_6): δ 0.14 (s, 18H), 2.0 (s, 4H) and 2.29 ppm (s, 3H). Anal.: Found: C, 53.10; H, 12.36; N, 7.09. $C_9H_{25}NSi_2$ calcd.: C, 53.12; H, 12.38, N, 6.88%.

1,3,3,5,5-Pentamethyl-3,5-disila-1-azacyclohexane (IV) was prepared analogously from a 1/0.45 mixture of $(BrH_2CSi(CH_3)_2)_2CH_2$ [17a] and methylamine in 79% yield: b.p. 341–342 K/27 mmHg; NMR ($DCCl_3$): δ -0.39 (s, 2H), -0.03 (s, 12H), 1.66 (s, 4H), 2.27 ppm (s, 3H). Anal.: Found: C, 51.00; H, 11.35; N, 7.21. $C_{18}H_{21}NSi_2$ calcd.: C, 51.27; H, 11.29; N, 7.41%.

The purity of all compounds was checked by gas chromatography.

Photoelectron spectra were recorded on a Perkin-Elmer PS 16 equipped with a heated inlet, and are calibrated with Xe ($^2P_{3/2}$: 12.13 eV) and Ar ($^2P_{3/2}$: 15.76 eV).

Electron spin resonance spectra were recorded on a Varian E 9 (frequency

9.5 GHz, 330 mT magnetic field, field modulation 100 kHz) and calibrated with Fremy's salt ($2a_N = 2.618$ mT).

Radical cation generation was best carried out in the ESR capillary under N_2 by adding to 1 mg amine 0.1 ml oxygen-free dry H_2CCl_2 and ca. 5 mg $AlCl_3$.

ESR simulation was carried out using the new program ESPLOT [17b]. The calculations were performed on the Univac 1108 of the Hochschul-Rechenzentrum Frankfurt.

Results and discussion

Photoelectron spectra

The PE spectrum of the title compound, $N(CH_2Si(CH_3)_3)_3$, is shown in Fig. 1 along with that of the isoelectronic hydrocarbon analogue, $HC(CH_2Si(CH_3)_3)_3$. For these large molecules, $C_{12}H_{33}NSi_3$ and $C_{13}H_{34}Si_3$, which contain 98 valence electrons and presumably because of fluctuating behaviour do not possess

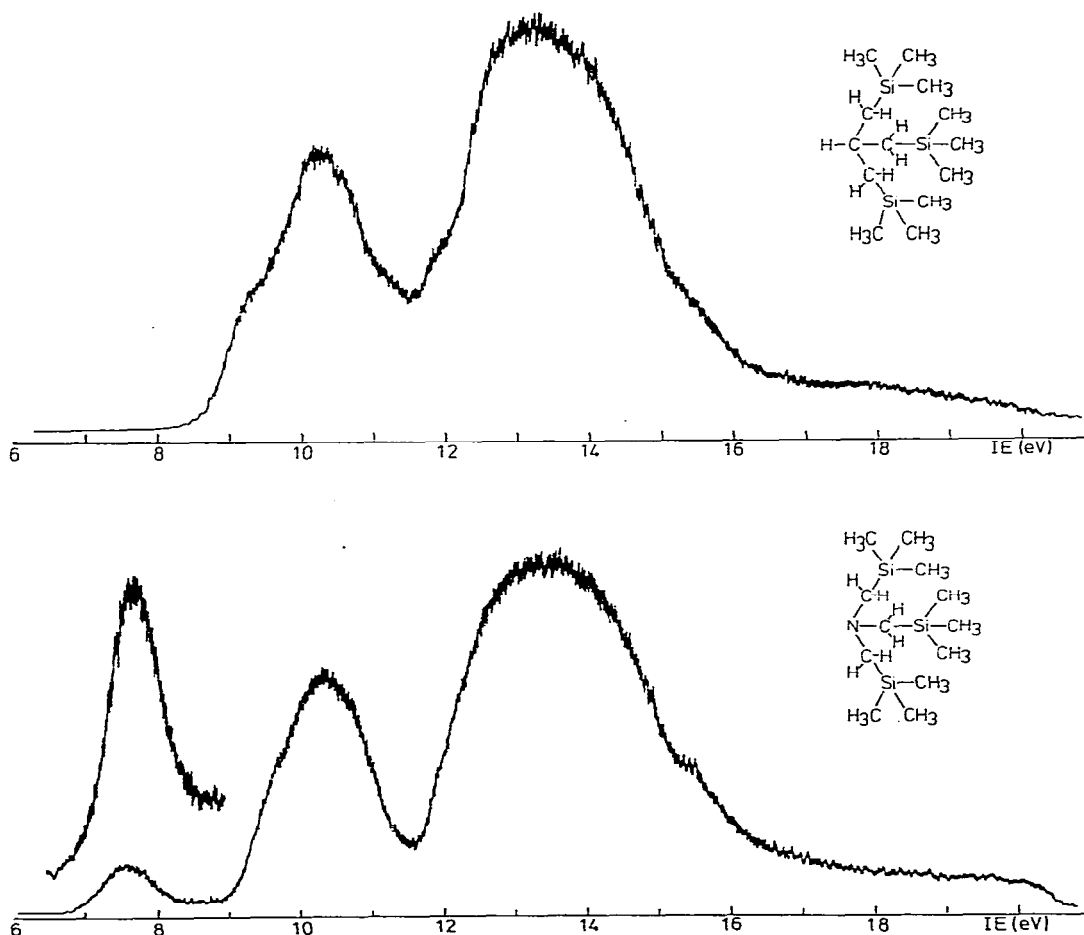
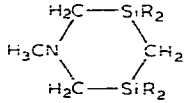
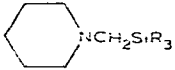
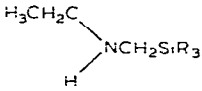
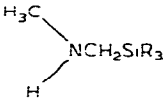


Fig. 1. He(I) photoelectron spectra of tris(trimethylsilylmethyl)-methane and -amine.

any definite structure of significant symmetry in the gas phase, molecular orbitals become meaningless [9]. An approximate assignment of their 49 Koopmans radical cation states can be made as follows. Usually, all ionizations of s -type electrons with main quantum numbers $n \geq 2$ are observed above 20 eV [18] (for carbon compounds cf. ref. 19) and, therefore, only 33 ionizations are expected within the helium(I) measurement region (Fig. 1). Radical cation state comparison between tris(trimethylsilylmethyl)amine and the isoelectronic methane derivative (Fig. 1) demonstrates that its low first ionization at only 7.66 eV (Table 1) must be of predominant nitrogen lone pair character. The PE band between 9 eV and 11.5 eV with a 10.5 eV maximum can be assigned to ca. 9 σ_{SiC} ionizations by comparison with the $\sigma_{\text{SiC}}(t_2)$ state of tetramethylsilane at $IE_1 = 10.57$ eV [20]. For the hydrocarbon, two additional $\sigma_{\text{CC}}(e)$ ionizations are expected around 12 eV, leading to the observed PE band broadening (Fig. 1). The corresponding σ_{NC} ionizations of the amine should occur only at higher energies, and therefore are probably hidden underneath the huge ionization hill between 12 eV and 17 eV, which comprises approximately 20 σ_{CH_n} radical

TABLE 1

VERTICAL FIRST IONIZATION POTENTIALS $IE_1^{\text{obs.}}$ (eV) AND VALUES $IE_1^{\text{calc.}}$ (eV) CALCULATED BY (2) FOR TRIMETHYLSILYLMETHYL-SUBSTITUTED AMINES

Compound		$IE_1^{\text{obs.}}$ (eV)	$IE_1^{\text{calc.}}$ (eV) ^a
$\text{N}(\text{CH}_2\text{SiR}_3)_3$	I	7.66	7.67
$\text{H}_3\text{CH}_2\text{CN}(\text{CH}_2\text{SiR}_3)_2$	II	7.82	7.85
$\text{H}_3\text{CN}(\text{CH}_2\text{SiR}_3)_2$	III	7.86	7.92
	IV	7.90	7.92 ^b
$(\text{H}_3\text{CH}_2\text{C})_2\text{NCH}_2\text{SiR}_3$	V	7.93	8.03
	VI	8.18	8.03 ^c
$(\text{H}_3\text{C})_2\text{NCH}_2\text{SiR}_3$	VII	8.20	8.17
$\text{HN}(\text{CH}_2\text{SiR}_3)_2$	VIII	8.36	8.35
	IX	8.46	8.53
	X	8.55	8.60
$\text{H}_2\text{NCH}_2\text{SiR}_3$	XI	9.07	9.03

^a Calculated using eq. 2. ^b Assuming 2 CH_2SiR_3 groups. ^c Assuming 2 CH_2CH_3 groups.

cation states. The first ionization energies of trimethylsilylmethyl-substituted amines (Table 1) decrease in energy in the substituent sequence $\text{CH}_2\text{Si}(\text{CH}_3)_3 > \text{CH}_2\text{CH}_3 > \text{CH}_3 > \text{H}$. This order, which has also been observed for the compounds (1), is reflected numerically by the parameters ΔIE_R in the perturbation equation

$$IE_1^{\text{calc.}} (\text{eV}) = \overline{IE}_R - \sum_R \Delta IE_R$$

$$= 9.71 - 0.68 n_{\text{CH}_2\text{SiR}_3} - 0.50 n_{\text{CH}_2\text{CH}_3} - 0.43 n_{\text{CH}_3}$$
(2)

obtained by a least-square fit to the experimental ionization energies (Table 1). The resulting regression

$$IE_1^{\text{calc.}} (\text{eV}) = 0.329 + 0.961 IE_1^{\text{obs.}}$$
(3)

shows a standard deviation of only $SE = 0.07$ eV. The perturbation formula (2) also allows prediction of the vertical first ionization energies of dialkyl- and trialkyl-amines [21] (4):

Compound	$IE_1^{\text{obs.}} (\text{eV})$	$IE_1^{\text{calc.}} (\text{eV})$
$\text{N}(\text{CH}_2\text{CH}_3)_3$ [21a]	8.19	8.21
$\text{N}(\text{CH}_3)_3$ [21b]	8.44	8.42
$\text{HN}(\text{CH}_3)_2$ [21b]	8.97	8.85
H_2NCH_3 [21b]	9.64	— ^a
H_3N [21c]	10.85	— ^a

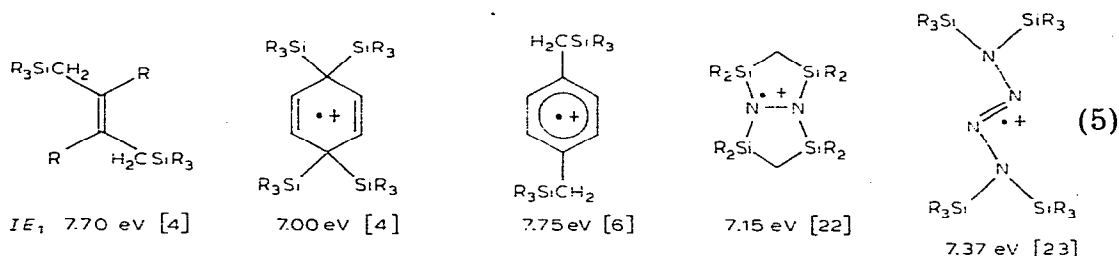
(4)

^a Not included in regression (3).

although the overall substituent effects on the nitrogen lone pair ionization are clearly not additive (cf. also Table 1).

Electron spin resonance spectra

The first ionization energies of numerous silicon substituted compounds, from which radical cations could be generated with AlCl_3 in H_2CCl_2 solution, e.g. (5): $\text{R} = \text{CH}_3$, suggest that the oxidation potential of the selective oxidi-



zing system corresponds to a vertical $IE_1 \leq 7.8$ eV [6]. Accordingly (Table 1), tris(trimethylsilylmethyl)amine can be oxidized to yield its aminium radical cation, $^+\text{N}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_3$, which is stable even at room temperature (Fig. 2).

The ESR spectrum of $^+\text{N}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_3$ at 180 K exhibits 25 lines and can

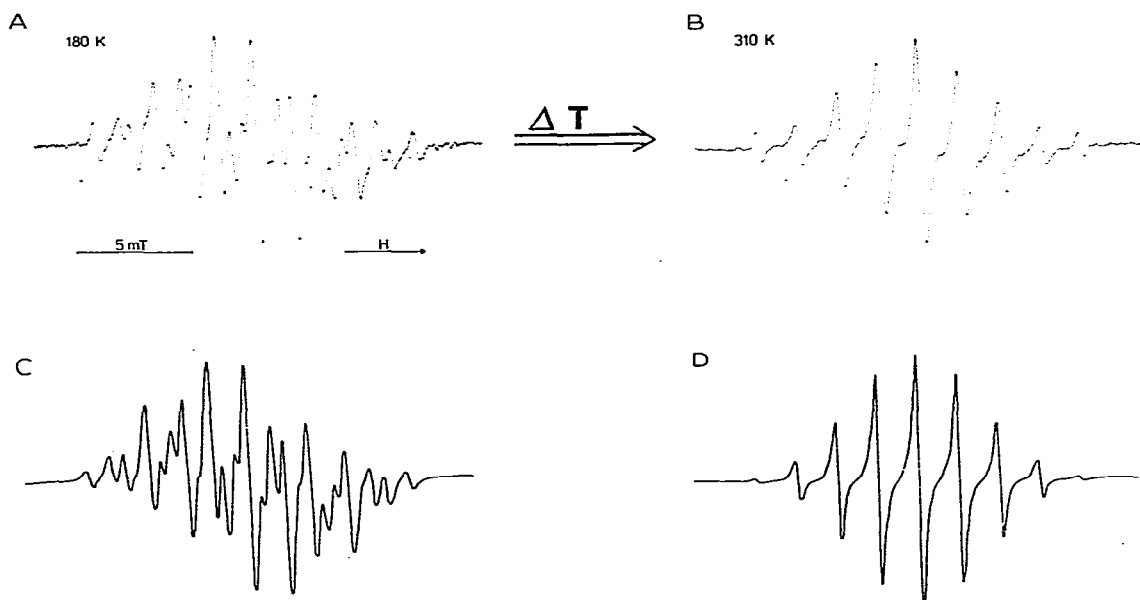


Fig. 2. ESR spectra of tris(trimethylsilylmethyl)aminium radical cation at 180 K (A) and at 310 K (B) as well as their best-fit computer simulations (C) and (D).

be simulated with the following set of coupling constants (Fig. 2C):

$$\begin{aligned}
 a_N &= 1.6 \text{ mT} & a_H &= 1.0 \text{ mT (2H)} & a_{29\text{Si}} &\sim 1.5 \text{ mT} \\
 & & & 1.6 \text{ mT (2H)} & & \\
 & & & 2.8 \text{ mT (2H)} & (a_H^{\text{SiR}_3} < 0.08 \text{ mT}) &
 \end{aligned} \tag{6}$$

The stability of the CH_2SiR_3 -substituted aminium radical cation permits study of the temperature dependence of its ESR signals: at 310 K only 9 lines with equal distances are observed (Fig. 2B). The ESR spectrum can be simulated with the assumption $a_N \sim a_H^{\text{CH}_2} = 1.8 \text{ mT}$ (Fig. 2D).

The 3 different proton couplings (6) found in the 180 K spectrum (Fig. 2A) suggest as preferred conformation:



The twist angle $\Delta\Theta$ can be calculated [17b] from the Heller/McConnell equa-

tion (9a) as follows:

$$\begin{aligned}
 a_{H,1} &= B_0\rho_N + B_2\rho_N \cos^2(\Theta - \Delta\Theta) \\
 a_{H,2} &= B_0\rho_N + B_2\rho_N \cos^2(\Theta + \Delta\Theta) \\
 \sin(2\Delta\Theta) &= \frac{a_{H,1} - a_{H,2}}{B_2 \times \rho_N \sin(2\Theta)} = \frac{2.8 \text{ mT} - 1.0 \text{ mT}}{5.7 \text{ mT} \times 0.77 \sin(2 \times 60^\circ)} \\
 \Delta\Theta &= 14^\circ
 \end{aligned}
 \tag{8}$$

The values inserted into eq. 7 are derived from the ESR data of $^{14}\text{N}(\text{CH}_3)_3$ [24a]: $B_2 = a_{\text{H}}^{\text{CH}_3} / \langle \cos^2\phi \rangle = 5.7 \text{ mT}$ and $\rho_N \sim a_{\text{N}}^{\text{CH}_2\text{X}} / a_{\text{N}}^{\text{CH}_3} = 0.77$.

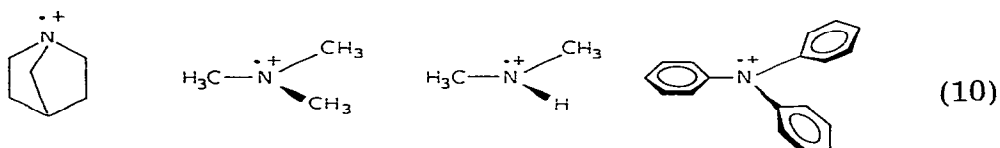
The proton coupling constants of $^{14}\text{N}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_3$ (6) and of $^{14}\text{N}(\text{CH}_3)_3$ ($a_{\text{H}}^{\text{CH}_3} = 2.85 \text{ mT}$ [24a]) provide information on the structure in solution. Based on the Heller/McConnell equation [27] (9a) a value R [28] can be determined from the averaged proton coupling (6) on the assumption that the constant B_0 is small compared to the constant B_2 :

$$a_{\text{H}} = (B_0 + B_2 \cos^2\Theta)\rho_N \tag{9a}$$

$$R = \frac{\langle \cos^2\Theta \rangle}{0.5} = \frac{\overline{a_{\text{H}}^{\text{CH}_2\text{X}}}}{a_{\text{H}}^{\text{CH}_3}} \frac{\rho_{\text{N}}^{\text{CH}_3}}{\rho_{\text{N}}^{\text{CH}_2\text{X}}} \approx \frac{\overline{a_{\text{H}}^{\text{CH}_2\text{X}}}}{a_{\text{H}}^{\text{CH}_3}} \frac{a_{\text{N}}^{\text{CH}_3}}{a_{\text{N}}^{\text{CH}_2\text{X}}} \approx \frac{1.8 \text{ mT}}{2.85 \text{ mT}} \frac{2.07 \text{ mT}}{1.6 \text{ mT}} = 0.82 \tag{9b}$$

The ratio $R = 0.82$ obtained (9b) is the largest found so far for R_3SiCH_2 substituted radicals [29], and indicates (relative to the values $R = 1$ for free rotation or $R = 0.5$ for complete blocking [28]) only slight steric interference by the bulky groups CH_2SiR_3 .

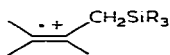
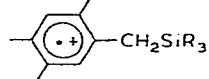
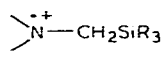
Comparison of the nitrogen coupling constant with those of the rather unstable trialkyl derivatives [24] and those of the aryl aminium radical cations [25], e.g. (10)



$a_{\text{N}} \text{ (mT)}$	3.02 [24a]	2.07 [24a]	1.92 _B [24b]	1.016 [25]
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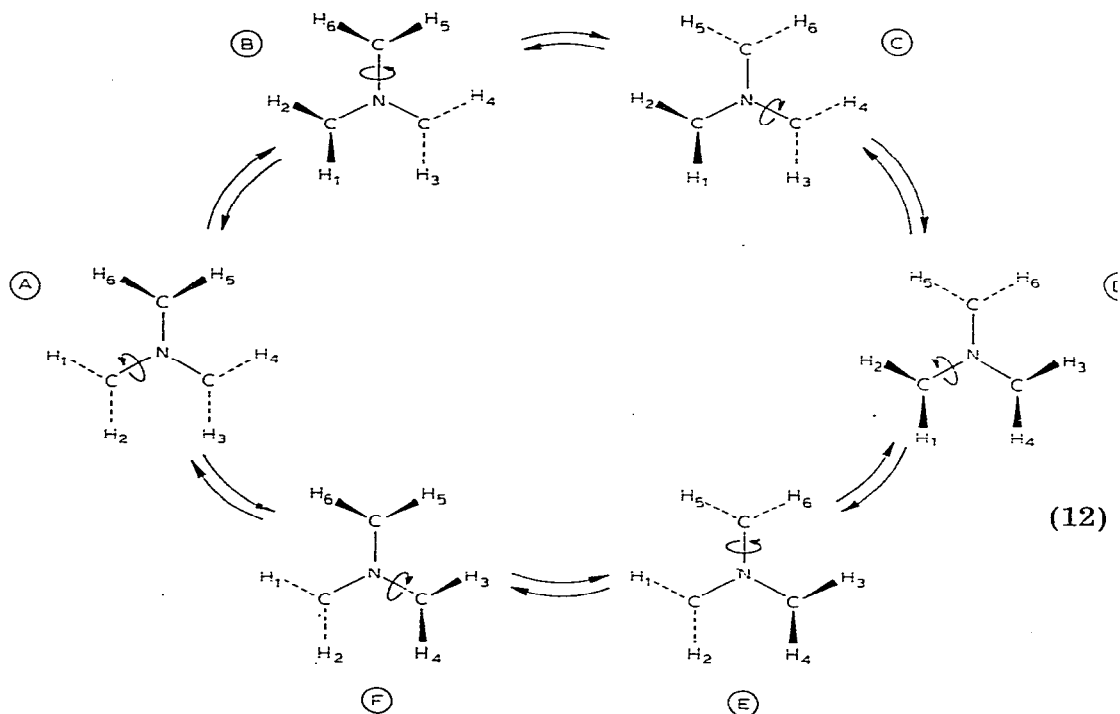
confirms that the tris(trimethylsilylmethyl)aminium radical cation must also contain a planar C_3N skeleton, and that the spin of the unpaired electron is considerably delocalized into $\sigma_{\text{C-Si}}$ bonds. It also should be pointed out, that the ratio of the coupling constants $a_{29\text{Si}}^{\text{CH}_2\text{Si}} / a_{\text{H}}^{\text{CH}_2\text{Si}}$ for substituents $-\text{CH}_2\text{SiR}_3$ ($\text{R} = \text{CH}_3$) decreases with increasing effective nuclear charge of the center of substitution (11).

The remarkable temperature dependence of the tris(trimethylsilylmethyl)aminium radical cation ESR spectrum may be interpreted qualitatively by selective line-width broadening [30] caused by the rotational interconversion among 6 individual conformations (cf. (12): $\rightleftharpoons \text{A} \rightleftharpoons \text{B} \rightleftharpoons \text{C} \rightleftharpoons \text{D} \rightleftharpoons \text{E} \rightleftharpoons \text{F} \rightleftharpoons$) of.

Species	Ref.	$a_{29\text{Si}}$	$a_{\text{H}}^{\text{CH}_2\text{Si}}$	$a_{29\text{Si}}/a_{\text{H}}^{\text{CH}_2\text{Si}}$
$\text{H}_2\dot{\text{C}}-\text{CH}_2\text{SiR}_3$	26	3.74	1.768	2.12
	4	1.25	0.79	1.58
	6	0.825	0.579	1.42
		1.5	1.8	0.83

(11)

equal probability 1/6. A further assumption concerns the planar C_3N^+ skeleton. Whereas at the low temperature of 180 K a 25 line spectrum corresponding to 3 sets of 2 equivalent protons plus 1 nitrogen is observed, on warming up of the sample the proton coupling averages to 1.8 mT (cf. (6): $(1.6 + 1.0 + 2.8 \text{ mT})/3 = 1.8 \text{ mT}$) at 310 K (Fig. 2B). At intermediate temperatures, all lines except $M_{\text{H}} = 0 \pm 3$ should be broadened. At 278 K the ESR spectrum actually consists of 9 sharp lines, and is consequently assigned to $M_{\text{H}} = 3, 0, -3$ with $M_{\text{N}} = 1, 0, -1$, respectively. On complete averaging, the relative intensity ratio of the central line ($M_{\text{H}} = 0, M_{\text{N}} = 0$) to the outermost ones ($M_{\text{H}} = 3, -3$ and $M_{\text{N}} = 1, -1$) should amount to 50 : 1 for 6 equivalent H and 1 N with the same hyperfine splitting. The ratio 7 : 1 observed at 310 K (Fig. 2B) shows that the interconversion is not fast enough to reach complete averaging within

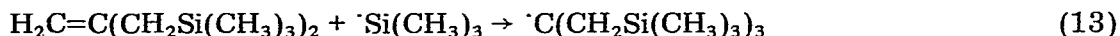


(12)

the ESR time scale even above room temperature. The increase of the nitrogen coupling constant from 1.6 mT at 180 K to 1.8 mT at 310 K can possibly be attributed to the increased out-of-plane bending deformation of the planar C_3N^+ skeleton.

Concluding remarks

The isoelectronic ($^+N \rightarrow ^+C$) carbon-centered radical has been generated by the following reaction [31]:



Its ESR spectrum exhibits a septet with $a_{H\beta} = 1.70$ mT, which corresponds to those reported for $H_2C^+CH_2Si(CH_3)_3$ with $a_{H\beta} = 1.78$ mT [32] and also for $((H_3C)_3C)_2C^+CH_2Si(CH_3)_3$ with $a_{H\beta} = 1.567$ mT [33]. This correlation indicates that the radicals prefer the conformation:



Since the β -hydrogen hyperfine splittings for these radicals are virtually temperature-independent, the temperature dependence observed for the aminium radical in the present study is quite remarkable. Presumably, steric hindrance plays an important role: a model assuming extensive hyperconjugation between the cationic nitrogen and the σ_{SiC} bond could help to account for the rather high rotational barrier around the $>N-CH_2-$ bond.

In summary, observation of the stable fluctuating aminium radical cation $^+N(CH_2Si(CH_3)_3)_2$ is made possible by the low first ionization energy of the trimethylsilylmethyl-substituted amine $N(CH_2Si(CH_3)_3)_3$. The general requirement for achieving low ionization potentials, viz. high electron density in the molecular ground state e.g. by introducing a centre of large effective nuclear charge as well as extensive delocalisation of the cationic charge after electron removal e.g. by donor substituents, should provide a useful guide for the design of other potentially persistent [33] radical cations.

Acknowledgements

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