

## Electron Paramagnetic Resonance Study on Some Alkylsilane Radical Cations in $\gamma$ -Irradiated $\text{CF}_3\text{CCl}_3$ Matrices

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Radical cations of ethyl-, propyl-, butyl-, ethylmethyl-, propylmethyl- and diethyl-silanes in  $\text{CF}_3\text{CCl}_3$  matrices at 77 K give two-line EPR spectra with separations of around 6 mT, independently of chain lengths and silicon positions. From results on some deuteriated alkylsilanes, and with INDO-MO calculations, it is concluded that each of the two-line spectra is attributable to the hyperfine coupling of the  $\beta$ -*trans* proton ( $\beta\text{-H}_{\text{trans}}$ ) with respect to the slightly elongated  $\alpha$ -carbon-silicon ( $\text{C}_\alpha\text{-Si}$ ) bond, where an unpaired electron is mainly confined. The *anti* configuration of the  $\text{Si-C}_\alpha\text{-C}_\beta\text{-H}_{\text{trans}}$  bond sequence is caused by maximization of the hyperconjugative effect between the unpaired electron localized in the  $\text{C}_\alpha\text{-Si}$  bond and the  $\text{C}_\beta\text{-H}_{\text{trans}}$  bond.

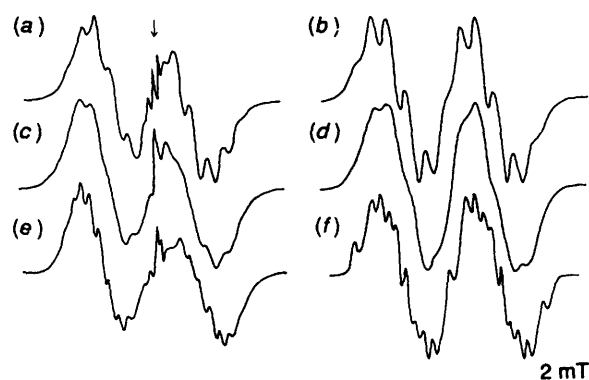
The structures and reactions of several kinds of organic radical cations produced by ionizing radiation have been extensively investigated, especially, by the EPR detection combined with a halocarbon-matrix isolation method.<sup>1,2</sup> EPR spectra of *n*-alkane radical cations, which are among the most fundamentally important radical cations, are characterized by two in-plane end-proton hyperfine couplings (hfs's) induced by unpaired electrons delocalized over the entire *trans-trans* carbon skeletons.<sup>3,4</sup>

Although silicon is in the same column of the periodic system as carbon, some properties of the two elements, such as the abilities to stabilize carbenium ions<sup>5</sup> differ widely. Consequently, silicon substitution on carbon atoms in *n*-alkane radical cations is likely to change the electronic and geometrical structures from those of the unsubstituted cations. Furthermore, the structures of linear cations without ring strain are expected to be sensitive to silicon-substitution effects. In the present study we report analyses of EPR spectra of silicon-substituted propane, butane and pentane radical cations produced in  $\gamma$ -irradiated  $\text{CF}_3\text{CCl}_3$  matrices, using some deuteriated alkylsilanes and with the aid of INDO-MO calculations, and discuss how the silicon substitution affects the cation structures.

### Experimental

Alkylsilanes were obtained by  $\text{LiAlH}_4$  reduction of the corresponding alkylchlorosilanes from Shinetsu Silicon according to the literature procedure.<sup>6</sup> In the synthesis of diethyldideuterosilane [ $(\text{C}_2\text{H}_5)_2\text{SiD}_2$ ]  $\text{LiAlD}_4$  was used as the reducing agent.  $[1,1,2,2,2\text{-}^2\text{H}_5]\text{-}$  and  $[1,1\text{-}^2\text{H}_2]\text{-ethylsilanes}$  ( $\text{C}_2\text{D}_5\text{SiH}_3$  and  $\text{CH}_3\text{CD}_2\text{SiH}_3$ ) were synthesized by the addition of tetrachlorosilane to Grignard reagents from  $[1,1,2,2,2\text{-}^2\text{H}_5]\text{ethylbromide}$  (MSD Isotopes with 99 atom% D) and  $[1,1\text{-}^2\text{H}_2]\text{ethyl bromide}$ , respectively, followed by  $\text{LiAlH}_4$  reduction.  $[1,1\text{-}^2\text{H}_2]\text{Ethyl bromide}$  was prepared by  $\text{LiAlD}_4$  reduction of acetyl chloride followed by bromination of  $[1,1\text{-}^2\text{H}_2]\text{ethyl alcohol}$ . The isotopic purities of  $\text{CH}_3\text{CD}_2\text{SiH}_3$  and  $(\text{C}_2\text{H}_5)_2\text{SiD}_2$  were 80.4% and over 99%, respectively. The alkylsilanes, except for ethylsilanes, were fractionally distilled and stored over molecular sieve 13X under vacuum lines. Their purities were over 99% from gas chromatographic analyses by the use of a 50-m capillary column. Gaseous ethylsilanes were purified by a trap-to-trap distillation method.  $\text{CF}_3\text{CCl}_3$  from Aldrich Chemical Co. with 99% purity was used as received.

EPR samples were prepared by the distillation of measured

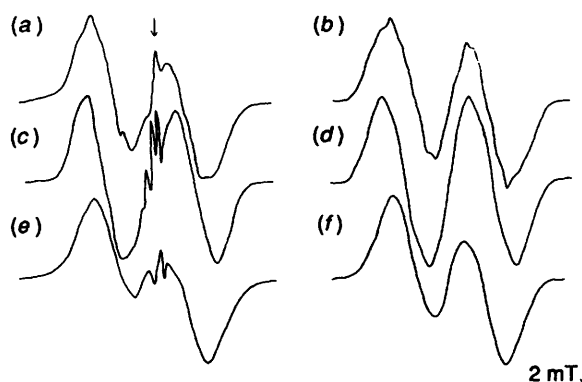


**Fig. 1** EPR spectra of ethylsilane (a), propylsilane (c) and butylsilane (e) cations in  $\text{CF}_3\text{CCl}_3$  matrices; calculated spectra of ethylsilane (b), propylsilane (d) and butylsilane (f) cations. In the observed spectra the peaks indicated by arrows are mainly due to spurious signals arising from imperfect subtraction of the matrix radicals and colour centres. The linewidths of the calculated spectra were taken to be 1.27 mT for (b), 1.47 mT for (d) and 0.67 mT for (f).

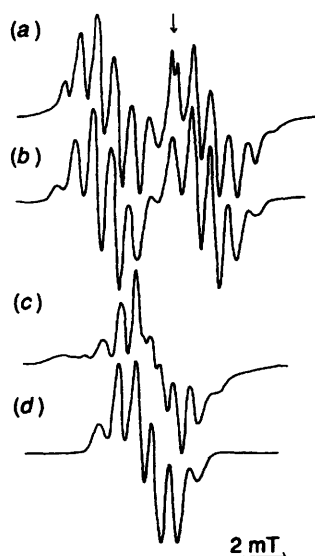
amounts of alkylsilanes and  $\text{CF}_3\text{CCl}_3$  into quartz EPR tubes on a vacuum line. The concentrations of alkylsilane solutes were about 0.3 mol%. The EPR samples were  $\gamma$ -irradiated with a  $^{60}\text{Co}$  source at 77 K to a dose of ca. 7 kGy. EPR spectra were measured at 77 K using an FE-1X JEOL spectrometer with 100 kHz field modulation. The EPR signals obtained at an interval of (50/8191)mT were digitized by a 12-bit A/D converter and fed to an NEC PC-9801 microcomputer. To obtain cation signals free from background signals arising from matrix radicals and radicals produced in the quartz EPR tubes, difference spectra between  $\text{CF}_3\text{CCl}_3$  with and without solutes were taken by the use of the computer. Simulation of EPR spectra was performed using the computer. Gaussian lineshapes and isotropic hyperfine couplings were assumed. INDO-MO calculations were carried out using the modified INDO program incorporating the parameters extended to second-row elements<sup>7</sup> into the original program.<sup>8</sup> Unless otherwise specified, the bond lengths and bond angles of alkylsilane radical cations used were the experimental values<sup>9</sup> of the neutral molecules.

### Results

*EPR Spectra of Alkylsilane Radical Cations.*—Observed EPR



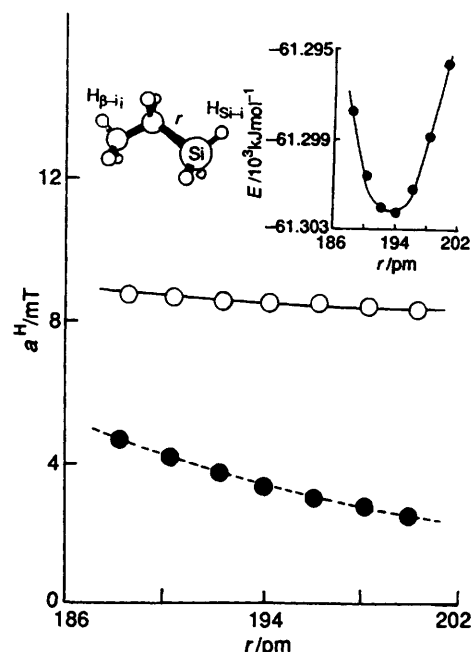
**Fig. 2** EPR spectra of ethylmethylsilane (a), propylmethylsilane (c) and diethylsilane (e) cations in  $\text{CF}_3\text{CCl}_3$  matrices; calculated spectra of ethylmethylsilane (b), propylmethylsilane (d) and diethylsilane (f) cations. In the observed spectra the peaks indicated by arrows are mainly due to spurious signals arising from imperfect subtraction of the matrix radicals and colour centres. The linewidths of the calculated spectra were taken to be 0.93 mT for (b), 1.26 mT for (d) and 1.71 mT for (f).



**Fig. 3** EPR spectra of  $[1,1\text{-}^2\text{H}_2]$ ethylsilane (a) and  $[1,1,2,2,2\text{-}^2\text{H}_5]$ ethylsilane (c) cations in  $\text{CF}_3\text{CCl}_3$  matrices; calculated spectra of  $[1,1\text{-}^2\text{H}_2]$ ethylsilane (b) and  $[1,1,2,2,2\text{-}^2\text{H}_5]$ ethylsilane (d) cations. In the observed spectra the peaks indicated by arrows are mainly due to spurious signals arising from imperfect subtraction of the matrix radicals and colour centres. The linewidths of the calculated spectra were taken to be 0.85 mT for (b) and 0.73 mT for (d).

spectra of ethyl-, propyl- and butyl-silane radical cations are shown in Figs. 1(a), 1(c) and 1(e), respectively. The spectra mainly consist of the two lines with separations of 6.30 mT for ethylsilane ( $\text{C}_2\text{H}_5\text{SiH}_3$ ) cation, 5.84 mT for propylsilane ( $\text{C}_3\text{H}_7\text{SiH}_3$ ) cation and 7.25 mT for butylsilane ( $\text{C}_4\text{H}_9\text{SiH}_3$ ) cation. Each of the two lines of the  $\text{C}_2\text{H}_5\text{SiH}_3$  cation further splits to at least four lines with an average separation ( $a_{\text{AV}}$ ) of 1.28 mT and that of  $\text{C}_4\text{H}_9\text{SiH}_3$  cation splits to at least six lines with an  $a_{\text{AV}}$  of 0.74 mT. In the two lines of the  $\text{C}_3\text{H}_7\text{SiH}_3$  cation some bumps are discernible.

EPR detection of isomer cations of  $\text{C}_2\text{H}_5\text{SiH}_3$ ,  $\text{C}_3\text{H}_7\text{SiH}_3$  and  $\text{C}_4\text{H}_9\text{SiH}_3$ , that is dimethylsilane, ethylmethylsilane ( $\text{C}_2\text{H}_5\text{SiH}_2\text{CH}_3$ ), propylmethylsilane ( $\text{C}_3\text{H}_7\text{SiH}_2\text{CH}_3$ ) and diethylsilane  $[(\text{C}_2\text{H}_5)_2\text{SiH}_2]$  cations, was also examined. For dimethylsilane, definite cation formation was hardly found. Figs. 2(a), 2(c) and 2(e) show the observed spectra of  $\text{C}_2\text{H}_5\text{SiH}_2\text{CH}_3$ ,  $\text{C}_3\text{H}_7\text{SiH}_2\text{CH}_3$  and  $(\text{C}_2\text{H}_5)_2\text{SiH}_2$  cations, respectively. These spectra also consist of two lines with



**Fig. 4** Proton hfs constant  $a^{\text{H}}$  and total energy  $E$  (inset) calculated for the ethylsilane cation by the INDO method plotted against  $\text{C}_\alpha\text{-Si}$  bond length  $r$ :  $\circ$ ,  $\text{C}_\beta\text{-H}_{\beta-i}$ ;  $\bullet$ ,  $\text{Si-H}_{\text{Si-i}}$

separations of 5.80 mT for  $\text{C}_2\text{H}_5\text{SiH}_2\text{CH}_3$  cation, 7.00 mT for  $\text{C}_3\text{H}_7\text{SiH}_2\text{CH}_3$  cation and 4.80 mT for  $(\text{C}_2\text{H}_5)_2\text{SiH}_2$  cation.

Since those two-line spectra were obtained with signal amplitudes comparable to those of the alkane-cation spectra, the two-line spectra could not be attributed to a  $^{29}\text{Si}$  hfs ( $I = 1/2$ , natural abundance of 4.70%). The hfs of one of protons attached to the silicon atom might be responsible for the two-line spectra. The spectrum of the  $(\text{C}_2\text{H}_5)_2\text{SiD}_2$  cation, however, gave almost an identical spectrum to the  $(\text{C}_2\text{H}_5)_2\text{SiH}_2$  cation, indicating negligible interaction of the unpaired electron with the deuterons attached to the silicon atom.

Fig. 3(a) shows the observed spectrum of the  $\text{CH}_3\text{CD}_2\text{SiH}_3$  cation. The multiplet structure is clearly discernible and the spectrum can be composed of 6 (an  $a_{\text{AV}}$  of 1.31 mT)  $\times$  2 (a separation of 6.81 mT) lines. The sextet shows an approximately binomial intensity ratio. The spectrum, therefore, is caused by six undeuterated proton hfs's; that of one proton gives the two lines separately 6.81 mT and those of five protons give the sextet structure. Two deuteron couplings of the cation decrease below the linewidth and are smeared out because  $a^{\text{D}} = 0.153a^{\text{H}}$ , where  $a^{\text{D}}$  and  $a^{\text{H}}$  are the deuteron and corresponding proton hfs constants. Close observation of the sextet, however, shows that the hyperfine couplings of the methylene proton are not negligibly small. Fig. 3(c) shows the observed spectrum of the  $\text{C}_2\text{D}_5\text{SiH}_3$  cation. The spectrum consists of six lines almost equally spaced with 1.27 mT. Some other unidentified lines are also present on the low field side. The observed spectral feature is similar to that of the spectrum caused by equivalent hyperfine couplings of one deuteron and three protons; the expected spectrum consists of six lines with an intensity ratio of 1:4:7:7:4:1. The three equal proton hfs's are assigned to those of the undeuterated protons of the  $\text{SiH}_3$  group and result from the free rotation of this group. Since one deuteron hfs is that of one of the methyl deuterons, the proton hfs giving the doublet spectra of  $\text{C}_2\text{H}_5\text{SiH}_3$  and  $\text{CH}_3\text{CD}_2\text{SiH}_3$  cations is unequivocally assigned to that of one of the methyl protons. Figs. 1(b), 3(b) and 3(d) show the calculated spectra with  $a^{\text{H}}$ 's of 7.04 mT (1 H) and 1.16 mT (2 H) for the methyl protons, 1.22 mT (2 H) for the methylene protons and 1.34 mT (3 H) for the protons of the  $\text{SiH}_3$  group. The  $a^{\text{D}}$  values were obtained by the relation  $a^{\text{D}} = 0.153a^{\text{H}}$ .

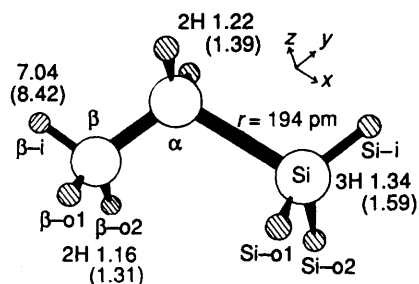


Fig. 5 Structure and proton hfs constants of ethylsilane cation; the hatched circles are the protons responsible for the observed hyperfine couplings and the calculated  $a^H$  values are shown in parentheses

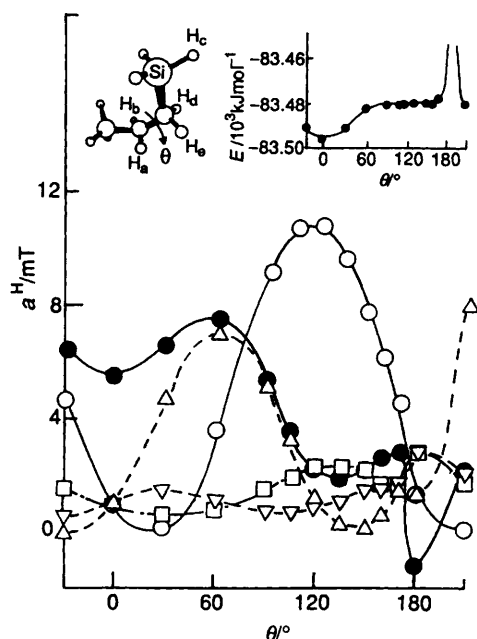


Fig. 6 Proton hfs constant  $a^H$  and total energy  $E$  (inset) calculated for the propylsilane cation by the INDO method against rotation angle  $\theta$  of the  $C_\alpha-C_\beta$  bond:  $\circ$ ,  $C_\beta-H_a$ ;  $\triangle$ ,  $C_\beta-H_b$ ;  $\bullet$ ,  $Si-H_c$ ;  $\nabla$ ,  $C_\alpha-H_d$ ;  $\square$ ,  $C_\alpha-H_e$ . The  $C_\alpha-Si$  bond length was taken to be 192 pm.

**Spectral Analyses with INDO-MO Calculations.**—Fig. 4 shows calculated  $a^H$ 's of the protons in positions  $\beta-i$  and  $Si-i$  of the ethylsilane cation as a function of the  $C_\alpha-Si$  bond length. The protons in the positions  $\beta-i$  and  $Si-i$  take the *trans* position with respect to the  $C_\alpha-Si$  and  $C_\alpha-C_\beta$  bonds, respectively, as shown in Fig. 5. Both of the two protons possess large  $a^H$  values, however, the  $a^H$  of the latter proton gradually decreases as the  $C_\alpha-Si$  bond length increases. At a  $C_\alpha-Si$  bond length of 194 pm, that is 7.4 pm longer than that of the neutral ethylsilane molecule, the total energy of the cation takes the minimum value, as shown in the inset of Fig. 4. The calculated  $a^H$  values at the bond length of 194 pm are given in parentheses in Fig. 5, with the assigned values. Since the  $SiH_3$  group rotates freely, as described before, the  $a^H$  values of the protons in this group were taken as the average of computed values for several configurations of the group.\* The calculated  $a^H$  values correspond well to the assigned values. Other structural changes such as that of the  $C_\alpha-C_\beta$  bond length and of the  $Si-C_\alpha-C_\beta$  bond angle were not able to give reasonable agreement with the assigned  $a^H$  values.

For the  $C_3H_7SiH_3$  cation two molecular forms are possible;

\* The cations of  $C_2H_5SiH_3$ ,  $C_3H_7SiH_3$  and  $C_4H_9SiH_3$  in  $CF_2BrCF_2Br$  matrices gave broad three-line EPR spectra with  $a_{AV}$ 's of around 6 mT. Assuming hindered rotation of the C-Si bond, one of the proton hfs's giving the three-line spectra might be attributable to that of the  $SiH_3$  group. Analysis of the spectra is in progress.

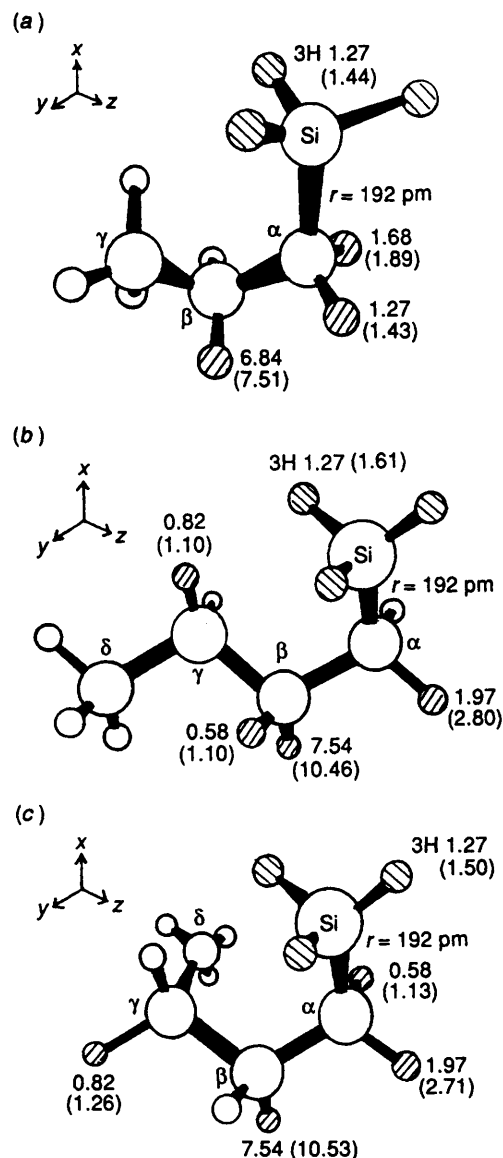


Fig. 7 Structures and proton hfs constants of propylsilane (a) and GT (b) and GG' forms (c) of butylsilane cations; the hatched circles are the protons responsible for the observed hyperfine couplings and the calculated  $a^H$  values are shown in parentheses

one is the *trans* (T) form where the  $Si-C_\alpha-C_\beta-C_\gamma$  bond sequence takes the *trans-trans* configuration and the other is the *gauche* (G) form in which the  $C_\alpha-Si$  bond occupies the *gauche* position with respect to the  $C_\beta-C_\gamma$  bond. Fig. 6 shows the changes in calculated  $a^H$  values when the  $C_\alpha-C_\beta$  bond rotates from the T form ( $\theta = 0^\circ$ ) to the G form ( $\theta = 120^\circ$ ). The  $C_\alpha-Si$  bond length was taken to be 192 pm because the total energies of the T, G and some other conformers showed minimum values at this bond length. The T form cation gives one of the protons in the  $SiH_3$  group an  $a^H$  value of 5 mT. However, the group presumably rotates as freely as in the ethylsilane cations and rotational averaging reduces the proton hfs by a factor of about three. Therefore, the T form cation is not responsible for the observed spectrum. At  $\theta = 150^\circ$  one of the protons attached to  $C_\beta$  possesses an  $a^H$  of 7.5 mT and  $a^H$ 's of other protons are less than 2 mT. The structure at  $\theta = 150^\circ$ , and the calculated  $a^H$  values are shown in Fig. 7(a). The proton with the  $a^H$  of 7.5 mT takes the place close to the *trans* position with respect to the  $C_\alpha-Si$  bond. Fig. 7(a) also shows that the  $C_3H_7SiH_3$  cation can be regarded as a methyl substituent of ethylsilane cation at the  $C_\beta-H_{\beta-o2}$  proton (Fig. 5). Fig. 2(d) is the calculated spectrum with the assigned  $a^H$  values given the numbers in Fig. 7(a).

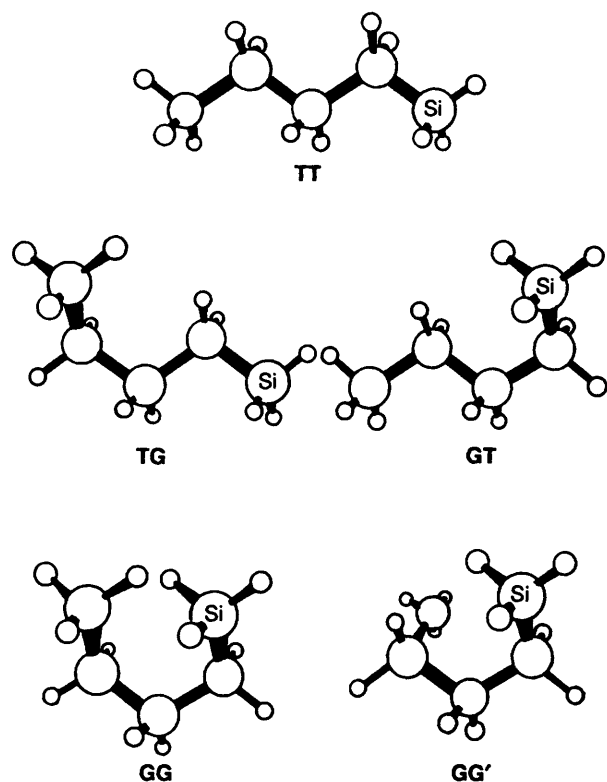


Fig. 8 Molecular forms of the butylsilane cation

For the  $C_4H_9SiH_3$  cation the five molecular forms shown in Fig. 8 are possible. Of the five forms and their intermediate conformers, the GT and GG' cations give reasonable explanations for the observed spectrum, and their structures and calculated  $a^H$  values are shown in Figs. 7(b) and 7(c). Here, the  $C_\alpha$ -Si bond lengths were taken to be 192 pm by reason of energy minimization, and the free rotation of the  $SiH_3$  group was presumed as is the case of ethylsilane and the  $C_3H_7SiH_3$  cation. The GT and GG' cations are ethyl substituents of the ethylsilane cation at the  $C_\beta$ - $H_{\beta-02}$  and  $C_\beta$ - $H_{\beta-01}$  protons, respectively, and give large  $a^H$  values to the protons at the  $\beta$ -i position of the ethylsilane cation. In the figures, the  $a^H$  values assigned on the basis of the calculated values are also given to the numbers. The calculated spectrum with the assigned values is shown in Fig. 2(e). At present, however, we do not know which form is responsible for the observed spectrum.

For disubstituted silane cations, that is  $C_2H_5SiH_2CH_3$ ,  $C_3H_7SiH_2CH_3$  and  $(C_2H_5)_2SiH_2$  cations, the calculations were carried out for the five forms shown in Fig. 8 and their intermediate conformers, of different bond lengths between silicon and the two adjacent carbon atoms. Figs. 9(a), 9(b) and 9(c) show cation structures explaining the observed spectra of the  $C_2H_5SiH_2CH_3$ ,  $C_3H_7SiH_2CH_3$  and  $(C_2H_5)_2SiH_2$  cations, respectively, and the calculated  $a^H$  values in parentheses. The  $C_\alpha$ -Si bond lengths were taken to be 194 pm, that is about 7 pm longer than those of the neutral molecules, from the energy minimization for each configuration. The configuration of the  $C_2H_5SiH_2CH_3$  cation is the T form which is the methyl substituent of ethylsilane cation at the  $Si-H_{Si-i}$  proton. The structure of the  $C_3H_7SiH_2CH_3$  cation is regarded as the conformer rotated  $60^\circ$  from the GG form to the TG form; the GG form is obtained by the methyl substitutions of the  $H_{Si-02}$  and  $H_{\beta-02}$  protons of the ethylsilane cation.  $(C_2H_5)_2SiH_2$  cation takes the GT form, which is the ethyl substituent of ethylsilane cation at the  $Si-H_{Si-02}$  proton. In the three cations the protons giving large  $a^H$  values take the  $\beta$ -trans positions with respect to the elongated  $C_\alpha$ -Si bonds. In Fig. 9 the assigned  $a^H$  values on considering the calculated values are also given to the numbers.

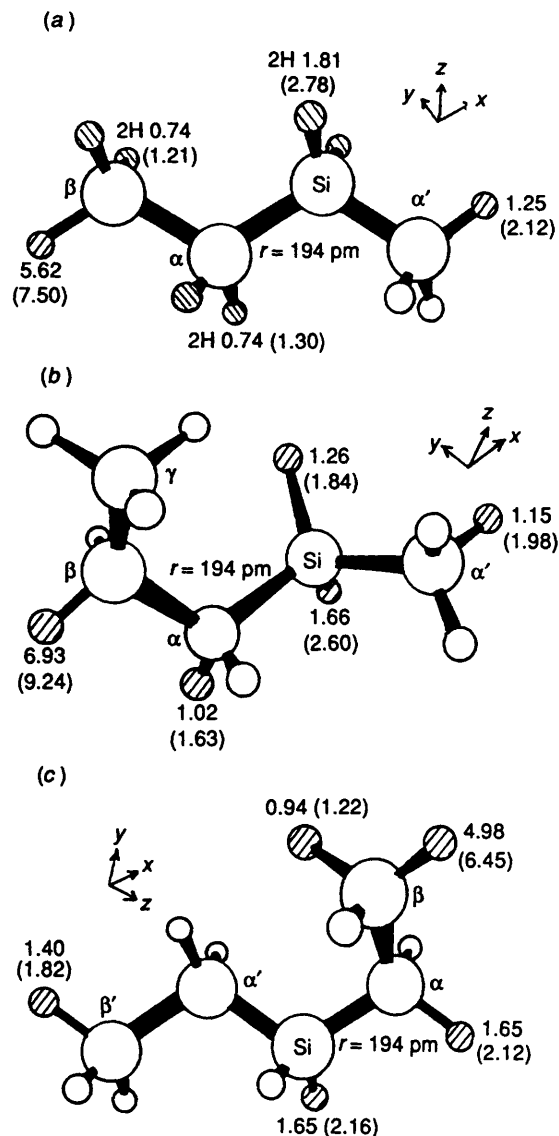


Fig. 9 Structures and proton hfs constants of ethylmethylsilane (a), propylmethylsilane (b) and diethylsilane (c) cations; the hatched circles are the protons responsible for the observed hyperfine couplings and the calculated  $a^H$  values are shown in parentheses

The calculated spectra with the assigned values for the  $C_2H_5SiH_2CH_3$ ,  $C_3H_7SiH_2CH_3$  and  $(C_2H_5)_2SiH_2$  cations are shown in Fig. 2(b), 2(d) and 2(f), respectively.

Tables 1 and 2 show spin and electron densities of the silicon and carbon atoms of the alkylsilane cations responsible for the observed spectra with the  $a^H$  values of  $\beta$ -protons giving the doublet structures. The  $x$ -axis was taken along the  $C_\alpha$ -Si bond and the  $y$ -axis was in the plane which contains the Si,  $C_\alpha$  and  $C_\beta$  atoms as shown in Figs. 5, 7 and 9. The spin densities of  $2p_y$  and  $2p_z$  orbitals were less than 0.03. The difference in the electron densities of the two orbitals was within 5% of the sum of the two densities. The unpaired electrons in all of the cations are mainly localized in the  $2p_x$  orbitals of the slightly elongated  $C_\alpha$ -Si bond, that is the  $p_\sigma$  orbital. The electron densities considerably decrease in the  $p_\sigma$  orbitals of the  $C_\alpha$  and Si atoms, especially in that of the Si atom.

## Discussion

The spectra of the alkylsilane cations examined are characterized by the two lines of the separations of around 6 mT independent of carbon numbers and silicon positions. Silicon unsubstituted  $n$ -alkane cations give 1:2:1 three-line spectra



**Table 1**  $\beta$ -Proton hyperfine coupling constants, spin densities of 2s and 2p<sub>x</sub> orbitals and electron densities of ethyl-, propyl- and butyl-silane radical cations

		Alkylsilane cation			
		$C_2H_5SiH_3^{+a}$	$C_3H_7SiH_3^{+b}$ (30° Rotamer from G form)	$C_4H_9SiH_3^{+b}$ GT form	$C_4H_9SiH_3^{+b}$ GG' form
$\beta$ -Proton hfs/mT					
	Obs.	7.04	6.84		7.54
	Calcd.	8.42	7.51	10.46	10.53
Spin density					
Si	2s	-0.013	-0.011	-0.014	-0.013
	2p <sub>x</sub>	0.267	0.257	0.246	0.235
C <sub><math>\alpha</math></sub>	2s	0.018	0.014	0.012	0.012
	2p <sub>x</sub>	0.413	0.382	0.351	0.343
C <sub><math>\beta</math></sub>	2s	-0.012	-0.010	-0.012	-0.012
	2p <sub>x</sub>	0.035	0.068	-0.051	0.050
C <sub><math>\gamma</math></sub>	2s		0.009	0.002	0.002
	2p <sub>x</sub>		0.003	0.012	0.012
C <sub><math>\delta</math></sub>	2s			-0.001	-0.001
	2p <sub>x</sub>			-0.001	0.000
Electron density					
Si	2s	0.962	0.956	0.958	0.957
	2p <sub>x</sub>	0.488	0.511	0.530	0.533
	2p <sub>y</sub> + 2p <sub>z</sub>	1.683	1.664	1.658	1.658
C <sub><math>\alpha</math></sub>	2s	1.111	1.115	1.114	1.113
	2p <sub>x</sub>	0.773	0.796	0.821	0.829
	2p <sub>y</sub> + 2p <sub>z</sub>	2.084	2.080	2.068	2.063
C <sub><math>\beta</math></sub>	2s	1.055	1.022	1.030	1.029
	2p <sub>x</sub>	0.916	0.911	0.878	0.878
	2p <sub>y</sub> + 2p <sub>z</sub>	1.988	1.990	2.024	2.023
C <sub><math>\gamma</math></sub>	2s		1.048	1.016	1.016
	2p <sub>x</sub>		0.948	0.952	0.946
	2p <sub>y</sub> + 2p <sub>z</sub>		1.943	1.946	1.975
C <sub><math>\delta</math></sub>	2s			1.045	1.047
	2p <sub>x</sub>			0.971	0.973
	2p <sub>y</sub> + 2p <sub>z</sub>			1.942	1.941

<sup>a</sup> The axis system and atomic indices are shown in Fig. 5 and the C <sub>$\alpha$</sub> -Si bond length was taken to be 194 pm. <sup>b</sup> The axis systems and atomic indices are shown in Fig. 7 and the C <sub>$\alpha$</sub> -Si bond lengths were taken to be 192 pm.

caused by hfs's of two in-plane end protons. The two-proton hfs constants decrease sharply with increase of carbon number in contrast to the case of the alkylsilane cations; the constants are 9.8 mT for the propane cation in SF<sub>6</sub> matrices, and 6.1 mT for the butane cation and 5.7 mT for the pentane cation in CF<sub>2</sub>ClCFCl<sub>2</sub> matrices.<sup>3</sup> The decrease of the hfs constants has been explained by the delocalization of unpaired electrons over entire carbon zig-zag chains.<sup>3,4</sup> In all of the alkylsilane cations, an unpaired electron is mainly confined in the p <sub>$\alpha$</sub>  orbital of the slightly elongated C <sub>$\alpha$</sub> -Si bond and induces a large hfs on the  $\beta$ -*trans* proton ( $\beta$ -H<sub>*trans*</sub>) in the Si-C <sub>$\alpha$</sub> -C <sub>$\beta$</sub> -H<sub>*trans*</sub> bond sequence of the *anti* configuration, as in the case of the ethylsilane cation. Therefore, the  $a^H$  values of the  $\beta$ -*trans* proton do not strongly depend on the carbon number and the silicon position.

The Si-C <sub>$\alpha$</sub> -C <sub>$\beta$</sub> -H<sub>*trans*</sub> bond sequence of the *anti* configuration is presumably related to the localization of the unpaired electron on the C <sub>$\alpha$</sub> -Si bond. Since the ionization potential ( $E_i$ ) of the sp<sup>3</sup> hybrid orbital and the electronegativity ( $\chi_p$  in the Pauling scale) of the silicon atom are lower than those of the carbon atom ( $E_i = 11.22$  eV\* and  $\chi_p = 1.8$  for Si;  $E_i = 13.85$  eV and  $\chi_p = 2.5$  for C<sup>10</sup>), the localization of unpaired electrons on the C <sub>$\alpha$</sub> -Si bond seems to be reasonable. An electrofugal effect of the silicon atom, that is inductive effect, could reduce the electron densities of the silicon s and p orbitals and enhance

their unpaired electron densities because the silicon atom combines with other atoms by its sp<sup>3</sup> hybrid orbitals. However, Tables 1 and 2 show that in the p <sub>$\alpha$</sub>  orbitals the unpaired electrons are mainly localized and the electron densities considerably decrease, but, the electron densities of the s and other two p orbitals are not so different from the unit value. Furthermore, the inductive effect of substituents is presumably independent of the conformations of substituents,<sup>11</sup> in contrast to the preference of the *anti* configuration of the Si-C <sub>$\alpha$</sub> -C <sub>$\beta$</sub> -H<sub>*trans*</sub> bond sequence in the alkylsilane cations. Therefore, the inductive effect of silicon atom does not play an important role in the determination of the electronic and geometrical structures of the alkylsilane cations.

In carbenium ions,  $\alpha$ -positive charges are strongly stabilized by  $\beta$ -substitution of electropositive substituents (X) such as silyl groups. The stabilization is essentially due to the hyperconjugative effect or the through-space electron delocalization between the C <sub>$\beta$</sub> -X bond and the vacant 2p orbital of the  $\alpha$ -positive carbon. The magnitude of the effect is at a maximum when the C-X bond is aligned with the empty 2p orbital.<sup>5,12</sup> In branched alkane cations an unpaired electron is rather confined in the p <sub>$\alpha$</sub>  orbital of one of the C-C bonds and induces large hfs's on  $\beta$ -*trans* protons with respect to the singly occupied C-C bond<sup>4,13,14</sup> as in the case of the alkylsilane cations. The hfs couplings of  $\beta$ -*trans* protons in branched alkane cations have been considered to be induced by the hyperconjugative mechanism.<sup>4,13</sup>

In radicals of bent structures an unpaired electron localized in

\* 1 eV =  $1.6021 \times 10^{-19}$  J.

**Table 2**  $\beta$ -Proton hyperfine coupling constants, spin densities of 2s and 2p<sub>x</sub> orbitals and electron densities of ethylmethyl-, propylmethyl- and diethylsilane radical cations

		Alkylsilane cation <sup>a</sup>		
		C <sub>2</sub> H <sub>5</sub> SiH <sub>2</sub> CH <sub>3</sub> <sup>+</sup> (T form)	C <sub>3</sub> H <sub>7</sub> SiH <sub>2</sub> CH <sub>3</sub> <sup>+</sup> (60° rotamer from GG form)	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiH <sub>2</sub> <sup>+</sup> (GT form)
$\beta$ -Proton hfs/mT				
	Obs.	5.62	6.93	4.98
	Calcd.	7.50	9.24	6.45
Spin density				
Si	2s	-0.024	-0.019	-0.035
	2p <sub>x</sub>	0.246	0.238	0.248
C <sub>α</sub>	2s	0.024	0.019	0.026
	2p <sub>x</sub>	0.417	0.392	0.399
C <sub>β</sub>	2s	-0.011	-0.011	-0.010
	2p <sub>x</sub>	0.022	0.036	0.014
C <sub>γ</sub>	2s		0.002	
	2p <sub>x</sub>		0.006	
C <sub>δ</sub>	2s	-0.001	-0.001	0.003
	2p <sub>x</sub>	0.014	0.013	0.035
C <sub>ε</sub>	2s			0.002
	2p <sub>x</sub>			0.026
Electron density				
Si	2s	0.959	0.956	0.981
	2p <sub>x</sub>	0.503	0.520	0.505
	2p <sub>y</sub> + 2p <sub>z</sub>	1.751	1.740	1.750
C <sub>α</sub>	2s	1.110	1.116	1.108
	2p <sub>x</sub>	0.776	0.793	0.787
	2p <sub>y</sub> + 2p <sub>z</sub>	2.078	2.073	2.077
C <sub>β</sub>	2s	1.053	1.022	1.052
	2p <sub>x</sub>	0.929	0.896	0.940
	2p <sub>y</sub> + 2p <sub>z</sub>	1.988	2.015	1.969
C <sub>γ</sub>	2s		1.047	
	2p <sub>x</sub>		0.963	
	2p <sub>y</sub> + 2p <sub>z</sub>		1.949	
C <sub>δ</sub>	2s	1.111	1.111	1.074
	2p <sub>x</sub>	0.993	0.994	1.029
	2p <sub>y</sub> + 2p <sub>z</sub>	2.021	2.019	1.958
C <sub>ε</sub>	2s			1.042
	2p <sub>x</sub>			0.941
	2p <sub>y</sub> + 2p <sub>z</sub>			1.942

<sup>a</sup> The axis systems and atomic indices are shown in Fig. 9 and the C<sub>α</sub>-Si bond lengths were taken to be 194 pm.

one of the bonds can interact with the bond aligned to the singly occupied bond by overlapping through space. The through-space interaction or the hyperconjugative effect is presumably dominant at  $\beta$ -positions. In bent hydrocarbon radicals, the interaction at the  $\beta$ -positions has been considered to be stronger in the front lobe side than in the back lobe side, because the overlap integral between C<sub>α</sub> and C<sub>β</sub> atoms in the former side is larger than that in the latter side.<sup>13</sup> Therefore, the *anti* configuration of the Si-C<sub>α</sub>-C<sub>β</sub>-H<sub>trans</sub> bond sequence in the alkylsilane cations is caused by the maximization of the hyperconjugative effect between the unpaired electron localized in the C<sub>α</sub>-Si bond and the C<sub>β</sub>-H<sub>trans</sub> bond. In the disubstituted silane cations two *anti* configurations including the silicon atom are possible and two large proton hfs's are expected in contrast to the observed result. Only one large proton hfs is responsible for one *anti* configuration, possibly caused by the greater distribution of the unpaired electron on the C<sub>α</sub> atom in the elongated C<sub>α</sub>-Si bond as shown in Tables 1 and 2. In the monosubstituted silane cations, one of the protons in the SiH<sub>3</sub> group which aligns to the C<sub>α</sub>-Si bond possesses a large *a*<sup>H</sup> value as shown in Fig. 4. The large proton hfs may be induced by through-space penetration of the unpaired electron localized largely on the C<sub>α</sub> atom. The full explanation, however, depends on further investigations.

In conclusion, the replacement of a carbon atom in *n*-alkane cations by a silicon atom forces the delocalized unpaired electron to push into the slightly elongated C<sub>α</sub>-Si bond; that is *n*-alkane cations are changed from the p<sub>σ</sub> delocalized type cation to the p<sub>σ</sub> localized type cation by the presence of a silicon atom in the skeleton. In the alkylsilane cations, the unpaired electron localized in the slightly elongated C<sub>α</sub>-Si bond interacts with the C<sub>β</sub>-H<sub>trans</sub> bond through the hyperconjugative mechanism and induces the large hfs on the  $\beta$ -*trans* proton.

Since submitting the present manuscript we have been made aware of a similar study, carried out independently, and recently accepted for publication (C. J. Rhodes, *J. Organomet. Chem.*, 1993, in the press). The conclusions reached are similar to our own, and do not invalidate any of the above discussion.

#### Acknowledgements

We thank Dr. M. Shiotani for helpful discussions.

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Paper 2/06840K

Received 24th December 1992

Accepted 5th February 1993