

## Alkyl and Silyl Derivatives of Benzene Radical-cations formed by Radiolysis: an Electron Spin Resonance Study

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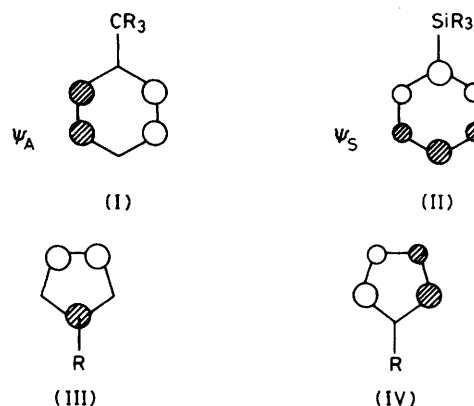
Exposure of dilute solutions of various alkyl- and silyl-benzenes in trichlorofluoromethane to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K gave species whose e.s.r. spectra are characteristic of substituted benzene cations. For the ethyl derivative large hyperfine coupling to the methyl protons establishes a preferred conformation in which the methyl group lies in the plane of the benzene ring. For the isopropyl derivative, and particularly for *p*-cymene cations, several conformers were detected, the sterically most favourable being the least stable. This is interpreted in terms of strong electron-donation from the C–H  $\sigma$ -orbitals into the ring  $\pi$ -orbital with is greater than that from C–Me  $\sigma$ -orbitals so that  $\pi$ -overlap with the C–H bonds is maximised. The energy difference is slightly greater than the steric energy differences. The SOMO for the silyl derivatives ( $\text{SiH}_3$ ,  $\text{SiHMe}_2$ , and  $\text{SiMe}_3$ ) is also the  $a_1$  orbital ( $\psi_s$ ) which places maximum spin-density on the position of the substituent. However, the degree of hyperconjugation involving Si–H  $\sigma$ -orbitals is reduced by a factor of *ca.* 2, as judged by the  $^1\text{H}$  hyperfine coupling constants. Nevertheless, it was not found necessary to invoke a mixture of the  $a_1$  and  $a_2$  orbitals ( $\psi_s$  and  $\psi_A$ ) to explain the results. These results are compared with those for the corresponding radical-anions and for the neutral cyclopentadienyl radicals.

The radical anions of corresponding alkyl- and silyl-benzenes make an interesting contrast since e.s.r. spectroscopy has clearly established that for the former the antisymmetric  $\pi$ -orbital ( $\psi_A$ ) (I) is favoured, whilst for the latter, the symmetric  $\pi$ -orbital ( $\psi_S$ ) (II) is the SOMO (semi-occupied molecular orbital).<sup>1–3</sup> This can be understood in part in terms of the greater  $\sigma$ - $\pi$  electron-donating strength of the  $\text{CR}_3$  group than the  $\text{SiR}_3$  group, and the ability of  $\cdot\text{SiR}_3$  groups to act as weak electron-acceptors *via* the appropriate  $3d$  orbital on silicon. The e.s.r. results and theoretical calculations suggest that slight thermal mixing of these orbitals occurs, the admixture of  $\psi_S$  being greater for  $(\text{PhCMe}_3)^-$  anions than for  $(\text{PhCH}_3)^-$  anions.

For the radical-cations of alkylated benzenes, the orbital selection is reversed, the  $\psi_S$  orbital being favoured, thereby encouraging electron delocalisation onto the alkyl group, *via* hyperconjugative delocalisation.<sup>4–7</sup> By analogy, it might have been expected that the silylbenzene cations would select the antisymmetric orbital ( $\psi_A$ ) as the SOMO. For the five-electron  $\pi$ -radicals derived from the neutral cyclopentadienyl radical, Davies and his co-workers have shown by e.s.r. spectroscopy that, as expected, alkyl substituents favour  $\psi_S$  (III), whilst  $\text{SiR}_3$  substituents do indeed favour  $\psi_A$  (IV), with some admixture of  $\psi_S$ .<sup>8</sup>

Results from photoelectron spectroscopy relating to the unrelaxed cations clearly establish that the first ionisation potential of a given alkylbenzene is appreciably less than that for the corresponding silyl derivative, and that the  $\pi_1$  and  $\pi_2$  orbitals are closer for the latter than the former.<sup>9–11</sup> However, from the spectra alone, it is not easy to judge which orbital ( $\psi_A$  or  $\psi_S$ ) lies lower for the silyl derivatives, although calculations at the MNDO/3 level suggest that the SOMO for the cations should be  $\psi_S$  rather than  $\psi_A$ .<sup>11</sup>

It has recently been established that exposure of dilute solutions of neutral substrates (S) in certain halogenated solvents such as trichlorofluoromethane to ionising radiation at low temperatures results in the formation of the parent cations ( $\text{S}^+$ ) or unimolecular breakdown products thereof, provided the ionisation potential of S is less than that of the solvent (*ca.* 11.8 eV for  $\text{CFCl}_3$ ).<sup>12–15</sup> Usually, the cations are free, but sometimes weak bonding occurs between  $\text{S}^+$  and a solvent molecule which manifests itself as a hyperfine coupling to a single chlorine nucleus.<sup>16,17</sup> We have used this technique to prepare various



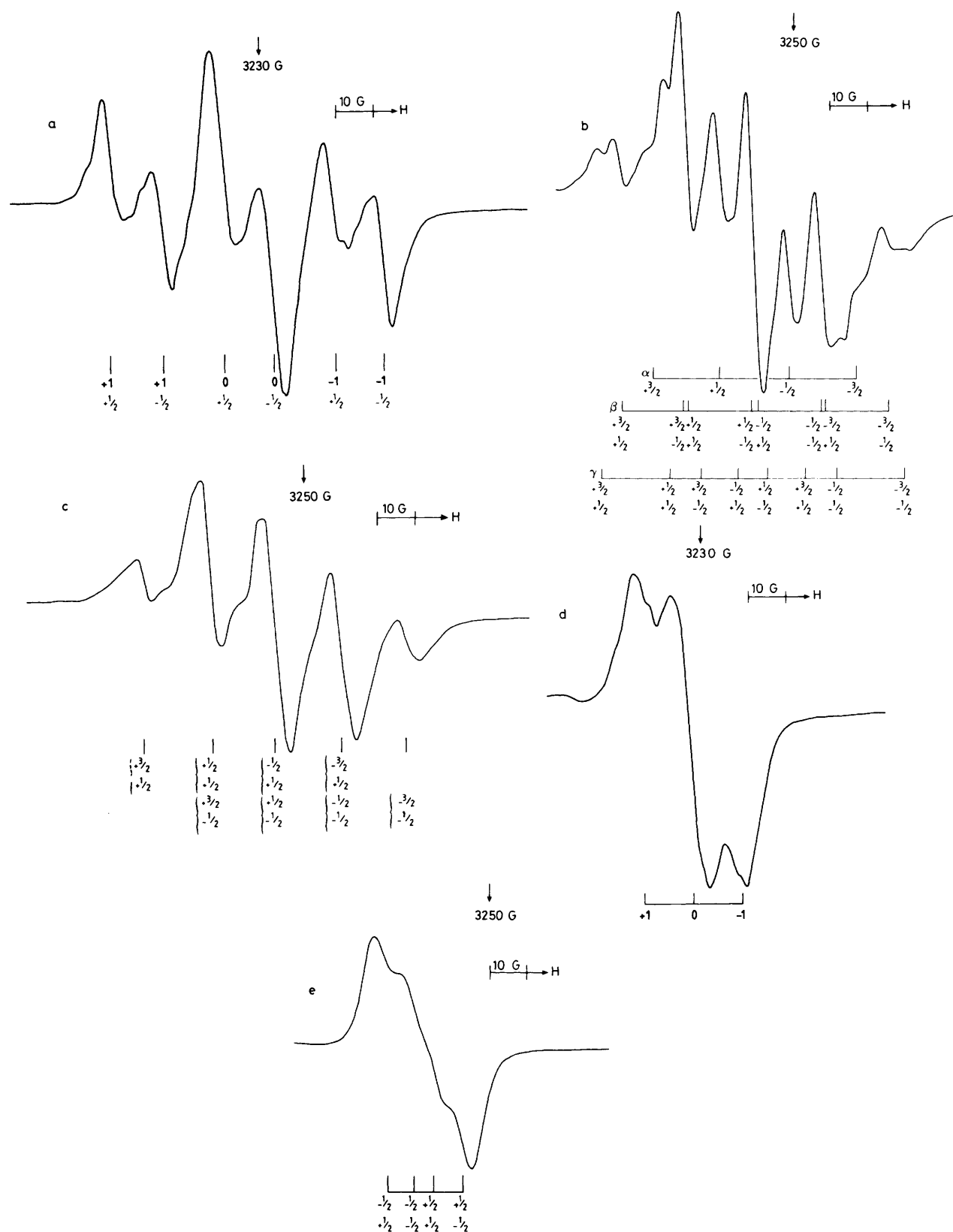
simple alkylbenzene cations, and, most significantly, Iwasaki and his co-workers have prepared the benzene cation and studied its tendency to distort at low temperatures.<sup>18</sup> Evidently distortion is marked, favouring a cation with  $D_{2h}$  symmetry with major spin-density on carbon atoms C-1 and -4 (*i.e.*  $\psi_S$ ). On annealing, the distortion becomes dynamic, giving six equivalent protons. It was this equilibrating form that we reported.<sup>7</sup> It is not clear why  $\psi_S$  should be completely favoured over  $\psi_A$  in this medium. Although not required by the Jahn–Teller theory, it is probable that similar distortions of the benzene rings occur for the substituted cations considered herein.

The main aim of the present study was to compare results for alkyl and corresponding silyl derivatives, and to determine if they share the same SOMO ( $\psi_S$ ) or if the relaxed silyl derivatives favour  $\psi_A$ .

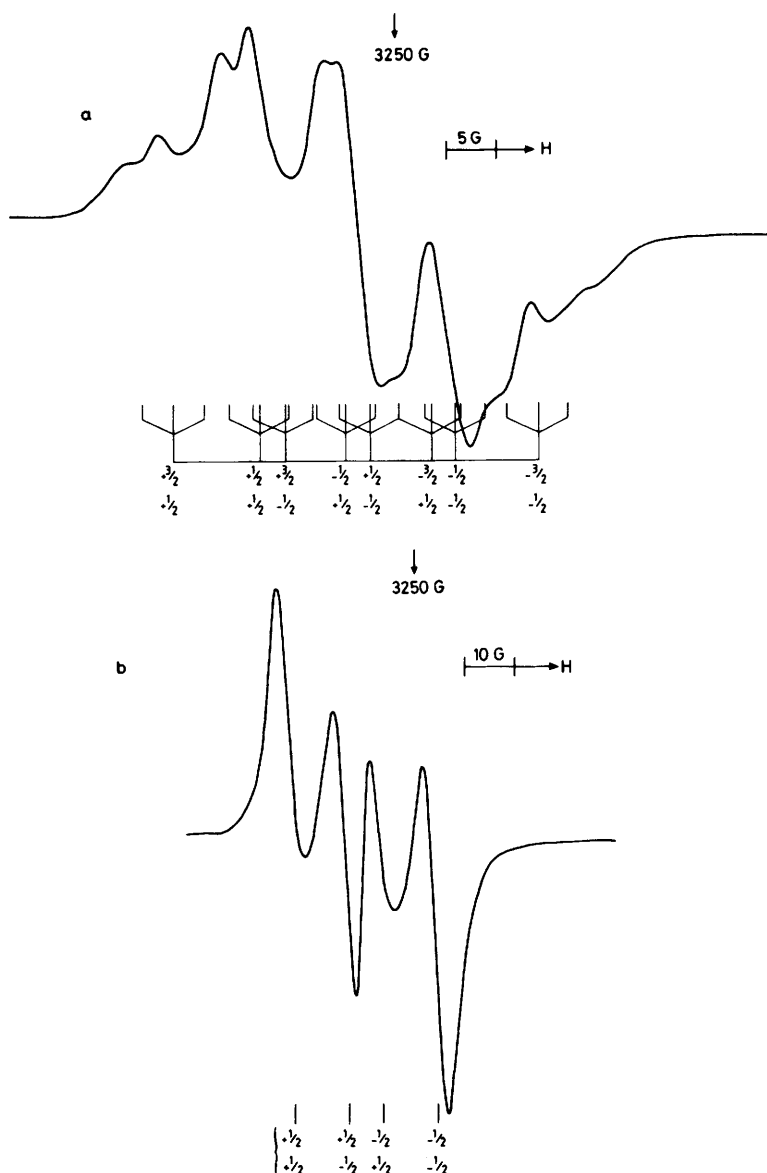
### Experimental

All materials were of the highest grade and were used as supplied. A range of solutions (0.01–0.05M) in Freon ( $\text{CFCl}_3$ ) was studied. Solutions were degassed by repeated freeze–thaw cycles, and were frozen at 77 K. These samples were exposed to  $^{60}\text{Co}$   $\gamma$ -rays in a Vickrad source for up to 1 h (*ca.* 1 Mrad).

E.s.r. spectra were measured at 77 K on a Varian E-109 spectrometer calibrated with a Hewlett–Packard 5246L



**Figure 1.** First-derivative X-band e.s.r. spectra for dilute solutions of a, ethyl benzene; b,c, *p*-cymene; and d,e, *t*-butyl benzene in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K, showing features assigned to  $(\text{C}_6\text{H}_5-\text{CH}_2\text{CH}_3)^+$  a, to  $[\text{CH}_3-\text{C}_6\text{H}_4-\text{CH}(\text{CH}_3)_2]^+$  b,c, and  $[\text{C}_6\text{H}_5-\text{C}(\text{CH}_3)_3]^+$  d,e. Spectrum b is that first obtained at 77 K.  $\alpha$ ,  $\beta$ , and  $\gamma$  centres have different conformations (see text). Spectrum c is the motionally averaged spectrum obtained at ca. 130 K. On recoiling to 77 K a spectrum similar to b was obtained, but features  $\alpha$  were absent, and  $\gamma$  had increased. Spectrum d shows the extra splitting for  $[\text{C}_6\text{H}_5-\text{C}(\text{CH}_3)_3]^+$  at 77 K which was lost on annealing e



**Figure 2.** First-derivative X-band e.s.r. spectra for dilute solutions of a,  $\text{PhSiH}_3$  and b,  $\text{PhSiH}(\text{CH}_3)_2$  in  $\text{CFCl}_3$  after exposure to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K, showing features assigned to  $(\text{PhSiH}_3)^+$  a and  $[\text{PhSiH}(\text{CH}_3)_2]^+$  b cations

frequency counter and a Bruker BH 12 E field probe, which were standardised with a sample of DPPH (diphenylpicrylhydrazyl). Samples were annealed by decanting the liquid nitrogen from the insert Dewar, and re-cooling whenever significant spectral changes were observed. In selected cases spectra were studied over a range of temperatures using a variable-temperature insert.

## Results

The e.s.r. spectra for toluene cations in Freon have been published previously (Figure 1 of ref. 7). Those for ethylbenzene cations and *p*-cymene cations are shown in Figure 1. That for isopropylbenzene was of similar quality to that for the ethyl derivative. The latter has been analysed in terms of two strongly coupled protons (29 G) and one weakly coupled proton (12 G), as indicated in the stick diagram. Analysis of the isopropyl derivative spectrum required the presence of two conformers

(Table), one with a small coupling to the  $\beta$ -proton (6 G) and one with a larger coupling (21 G), the latter being favoured. For *p*-cymene, a strong coupling to the *p*-methyl protons (18 G) together with coupling to one other proton is required to give a satisfactory fit, but three different conformers were formed at 77 K (Figures 1b and c). One, with zero coupling to the  $\beta$ -proton, was unstable, and was lost irreversibly on annealing. Another, with a large coupling (28 G), grew in intensity simultaneously. All three cations gave averaged spectra reversibly on annealing, the average  $\beta$ -proton coupling being close to that for the methyl protons of the toluene cation (18.5 G). However, the onset of averaging occurred at *ca.* 150 K for the ethyl derivative and *ca.* 130 K for the isopropyl derivatives.

The spectrum for the *t*-butyl derivative is more difficult to understand (Figures 1d and e). At 77 K a broad triplet was obtained (*A ca.* 13 G). On warming this changed to a quartet (Figure 1d) and then to the expected 12 G doublet. These changes were reversible. The doublet is clearly due to the *para*-

Table. E.s.r. parameters

Cation	<sup>1</sup> H hyperfine coupling (G) <sup>a,b</sup>	
	<i>para</i> -H	Substituent H
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> <sup>+</sup>	12	(3 H) 18.5
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>3</sub> <sup>+</sup>	12	(2 H) 29
C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	12	(1 H) (i) 6, (ii) 21
CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	(CH <sub>3</sub> ) 18	(1 H) (i) 0, (ii) 18, (iii) 28
C <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	12	c
C <sub>6</sub> H <sub>5</sub> SiH <sub>3</sub> <sup>+</sup>	11	(3 H) 9
C <sub>6</sub> H <sub>5</sub> SiH(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	11	(1 H) 18
C <sub>6</sub> H <sub>5</sub> Si(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	11	

<sup>a</sup> G = 10<sup>-4</sup> T (ca. ±0.25). <sup>b</sup> All *g*-values were close to 2.0025. The form of the spectra suggest slight *g*-anisotropy but this was too small to estimate with confidence. <sup>c</sup> Structure of unknown origin was observed at 77 K but was lost on annealing.

hydrogen; the source of the other splitting is not yet clear to us.

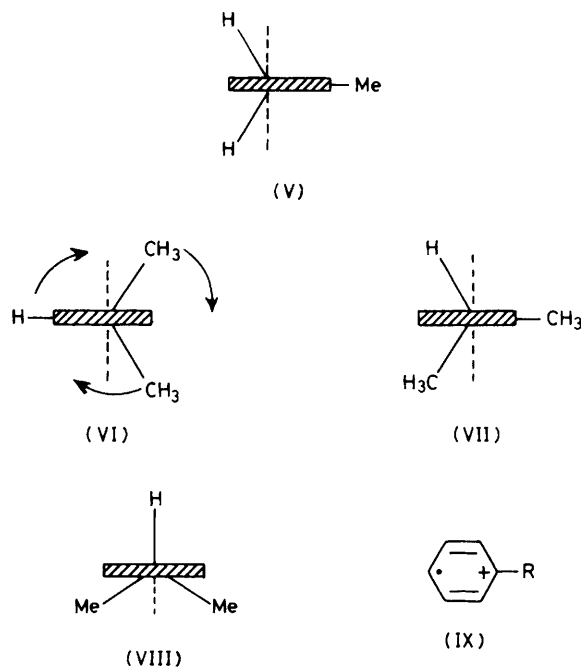
Spectra for the silyl derivatives (PhSiH<sub>3</sub>)<sup>+</sup> and (PhSiHMe<sub>2</sub>)<sup>+</sup> are shown in Figure 2. The former comprises a quintet (ca. 10 G) due to four nearly equally coupled protons, each feature resolving into a triplet (3 G) on annealing (Figure 2a). That for the SiMe<sub>3</sub> derivative is a simple doublet [*a*(<sup>1</sup>H) 11 G], whilst for the SiHMe<sub>2</sub> derivative two dissimilar doublet splittings are required (11 and 18 G) to explain the spectrum.

## Discussion

These results are all best interpreted in terms of the symmetric SOMO,  $\psi_s$ . Thus, the unique proton splitting of ca. 12 G for the alkyl derivatives and 11 G for the silyl derivatives is assigned to the *para*-ring protons. These coupling constants are appreciably larger than that reported for the *D*<sub>2h</sub> form of the benzene cation (8.2 G), despite delocalisation onto the substituents. One possible reason for this is given below. Coupling to the remaining ring protons is expected to be in the region of 2–3 G, but this was only clearly resolved for the silyl derivative, for two of the four protons, which are expected to be equivalent in pairs.

Results for the ethyl derivative are noteworthy in that coupling to the equivalent methylene protons (29 G) is very much greater than that (18.5 G) observed for the toluene cation.<sup>7</sup> This result requires that the conformation shown in (V) is adopted. This is surprising, since it is sterically the least favoured conformer. We suggest that hyperconjugative electron release for the C–H  $\sigma$ -bonds is markedly more favourable for this cation than is that from the C–CH<sub>3</sub> bond, and that this outweighs the steric barrier caused by the in-plane methyl group. It is, however, curious that some compromise structure of lower symmetry is not adopted. The spectrum changes quite sharply to that for a rotating ethyl group in the 150–160 K region [*A*(<sup>1</sup>H) 18.5 G].

For the two isopropyl derivatives (cumene and *p*-cymene) there seems to be an almost complete balance between the steric and hyperconjugation forces. Thus rotation is less hindered than for the ethyl derivative, and different conformations have comparable stabilities. At 77 K, one of the two major first formed species for *p*-cymene showed only an 18 G quartet due to hyperfine coupling to the methyl protons. However, this form was lost irreversibly on annealing. The other two species had  $\beta$ -proton splittings of ca. 18 and 28 G, respectively, and were both reformed from the averaging species on recooling to 77 K. We suggest that the species with *A*(<sup>1</sup>H)<sub>6</sub> ca. 0 has conformation (VI), this being the sterically favoured form of the parent molecules. The species with *A*(<sup>1</sup>H) 28 G must then have the structure (VII), the conformer having *A*(<sup>1</sup>H) ca. 18 G being



between these two structures. Clearly these structures have comparable stabilities, which explains why 'free' rotation sets in reversibly on annealing.

For the silyl derivative, the proton coupling for the SiH<sub>3</sub> group (9 G) is about half that obtained for the toluene cation (18.5 G). It is noteworthy that this reduction by a factor of 2 is exactly that observed on going from oxygen to sulphur for typical ether and sulphide cations, R<sub>2</sub>O<sup>+</sup> and R<sub>2</sub>S<sup>+</sup>.<sup>19–21</sup> In the present case, the major factor contributing to this fall is, in our view, the poor orbital overlap for the Si–H relative to the C–H orbital. However, for the ether and sulphide cations it is, we suggest, mainly the difference in the effective electron-affinity of the ether 2*p* and sulphur 3*p* orbitals that causes the reduction, so the similarity in the changes observed must be coincidental.

For the (PhSiHMe<sub>2</sub>)<sup>+</sup> cation the coupling of 18 G is assigned to the Si–H proton. The large coupling can be understood in terms of the conformer (VIII) giving maximum  $\sigma$ – $\pi$  overlap, and hence double the average coupling of 9 G observed for the SiH<sub>3</sub> derivative overlap. We therefore conclude that, as with carbon, electron release from the Si–H bond is more favourable than that from the Si–Me bonds. Nevertheless, it is clearly less than that for C–H bonds. For this cation, hyperconjugation dominates steric factors in controlling conformation, the latter being greatly reduced because of the size of the silicon atom. No change in conformation was observed on warming for this species, in marked contrast with the (PhCHMe<sub>2</sub>)<sup>+</sup> cation.

We now return to the reason why the *para*-proton coupling is so much greater than that found for C<sub>6</sub>H<sub>6</sub><sup>+</sup> cations at 4 K. This is not thought to be caused by slight admixture of  $\psi_A$  into the  $\psi_s$  structure for C<sub>6</sub>H<sub>6</sub><sup>+</sup>, and clearly, such admixtures for the substituted cations would require that the pure  $\psi_s$  structure should exhibit even larger *para*-proton coupling constants. We invoke our positive-charge spin-density separation concept previously outlined.<sup>7</sup> This depends upon the fact that electron donation from C–H (or Si–H)  $\sigma$ -bonds is encouraged by the positive charge. Thus there is a distortion of the wavefunction so as to place high positive charge-density on the carbon atom adjacent to the substituent, and, concomitantly, high spin-density on the remote *para*-carbon, as in (IX). Only a minor bias in favour of such an extreme is required to explain the

increase in  $A(^1\text{H})$  for the *para*-hydrogen. This also shows why the coupling is greater for the alkyl than for the silyl derivatives.

**Conclusions.**—The results demonstrate conclusively that the  $\psi_S$  structure is favoured by both alkyl and silyl derivatives. Hence for the alkyl derivatives there is a change from  $\psi_A$  to  $\psi_S$  on going from the anion to the cation radicals, whereas, for the silyl derivatives,  $\psi_S$  is favoured for both. The results from photoelectron spectroscopy suggest that for the unrelaxed form,  $\psi_S$  and  $\psi_A$  are very close together, but for the relaxed forms, we find no evidence for any admixture. This suggests that there is a considerable distortion of the ring, as observed for  $\text{C}_6\text{H}_6^{+18}$ .

We have also observed an interesting and unusual competition between steric and hyperconjugative forces in controlling the conformation of alkyl and silyl groups, which conclusively demonstrate the dominance of C–H hyperconjugation. This is very strong in these systems because of the positive charge effect. For the alkyl (but not the silyl) derivatives, rotation sets in reversibly on annealing. These systems could therefore be studied to give accurate energy barriers to rotation.

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