

The Cation of Hexamethyldistannane generated by Radiolysis: An E.S.R. Study

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Summary Analysis of the Sn hyperfine tensor components for $(\text{Me}_3\text{Sn}\cdot\text{SnMe}_3)^+$ generated by radiolysis of hexamethyldistannane in fluorotrichloromethane at 77 K shows that the metal-metal orbital is largely $4p_z + 4p_z$, the 4s contribution being negligible.

It seems probable that the long search for alkane cation radicals having well defined e.s.r. spectra is over. Our assignment¹ of a complex e.s.r. spectrum comprising 7 major hyperfine features to the cation of hexamethylethane, $[\text{Me}_3\text{C}\cdot\text{CMe}_3]^+$, has been strongly supported by Williams and co-workers² and by Shida and co-workers.³ We used hydrocarbon-tetrachloromethane systems, whereas the other two studies were conducted using solutions in Freon (Cl_3CF). We specifically selected the molecule $\text{Me}_3\text{C}\cdot\text{CMe}_3$ for study since it seemed probable that, following electron loss, the central carbon-carbon bond would stretch so that the 'hole' would become strongly localised in the C-C region. Furthermore, we suggested that the two halves of the molecule would tend towards local planarity, since $\text{Me}_3\text{C}\cdot$ radicals are planar, or nearly so. This key postulate has been criticised in both subsequent studies, a pyramidal conformation being favoured.^{2,3}

One important aspect of the e.s.r. spectrum for $[\text{Me}_3\text{C}\cdot\text{CMe}_3]^+$ ions is that there are six strongly coupled protons [$a(^1\text{H}) = 29 \text{ G}^2,^3$ or 32 G^1] and 12 weakly coupled protons. Our proposal involving a preferred alignment of six C-H bonds so as to give maximum overlap with the σ -orbital,¹ also favoured by others,^{2,3} seemed to us to support the near-planar configuration, since this naturally leads to steric restrictions. Furthermore, the total proton hyperfine coupling was shown to be slightly greater than that for $\text{Me}_3\text{C}\cdot$ radicals.¹ An increase is expected because of the positive charge effect for hyperconjugation⁴ whereas going from a planar to a pyramidal configuration leads to a decrease in such delocalisation. Hence again, the results seemed to us to favour a near-planar configuration at the two central carbon atoms.

The first one-electron σ -radical of this class to be studied by e.s.r. spectroscopy, $\cdot\text{B}_2\text{H}_6^-$, was also thought to be made up of nearly planar BH_3 units.⁶

This important structural issue would be nicely probed by suitable ^{13}C enrichment, but this has not yet proved possible. It occurred to us that useful information would be forthcoming if ^{29}Si , ^{73}Ge , or $^{117/119}\text{Sn}$ hyperfine features could be studied in the corresponding $(\text{Me}_3\text{Si}\cdot\text{SiMe}_3)^+$, $(\text{Me}_3\text{Ge}\cdot\text{GeMe}_3)^+$, or $(\text{Me}_3\text{Sn}\cdot\text{SnMe}_3)^+$ cations. Our attempts to detect ^{29}Si features for the di-silicon cation were unsuccessful, and two recent reports on these ions also show

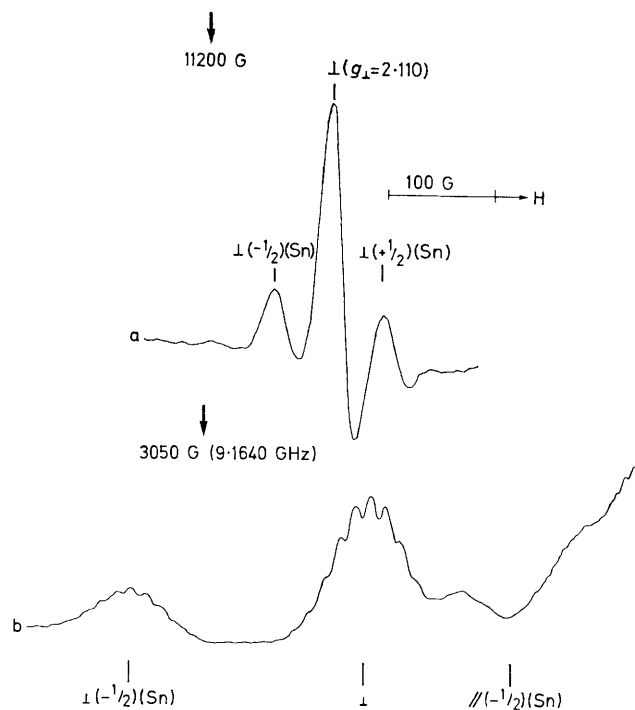


FIGURE. First derivative e.s.r. spectra for $(\text{Me}_3\text{Sn})_2$ in CFCl_3 after exposure to ^{60}Co γ -rays at 77 K showing features assigned to $(\text{Me}_3\text{Sn})_2^+$ cations: (a) Perpendicular features at Q-band. (b) Perpendicular features at X-band. Only the low field (\perp) features were resolved, the parallel features being hidden beneath intense free-spin signals (not shown). The proton hyperfine multiplet structure was not resolved in the Q-band spectrum.

no evidence for ^{29}Si coupling.^{3,7} However, I have been able to detect well defined coupling to $^{117/119}\text{Sn}$ for the di-tin cation, as indicated in the Figure. (^{117}Sn and ^{119}Sn have $I = \frac{1}{2}$, and such similar moments that their features superimpose in these spectra. Their joint natural abundance is 16.35%.) The Q -band spectrum shows the perpendicular features quite clearly, the satellite lines having the correct relative intensities for a radical containing two equivalent Sn atoms (Figure a). The proton hyperfine features are not resolved, but the g_{\perp} value is identical with that for the more intense multiplet detected in the X -band spectrum (Figure b). Unfortunately, the parallel features were obscured by features from other radicals, but an upper limit of *ca.* 400 G can be placed on the $^{117/119}\text{Sn}$ parallel coupling constant. The perpendicular X -band features show the $M_1 = -\frac{1}{2}$ $^{117,119}\text{Sn}$ component and probably also the $-\frac{1}{2}$ parallel component, as indicated in Figure b. These features are more intense than expected because the anisotropy of the $M_1 = -\frac{1}{2}$ line is much less than that for the main features for radicals containing non-magnetic isotopes. (This is based on the assumption that $g_{\parallel} = 2.002$, as found for the di-germanium cation.⁹) Similarly, the $M_1 = +\frac{1}{2}$ (high-field) features are expected to have a far greater anisotropy and hence should be correspondingly weak. This explains why the $+\frac{1}{2}$ perpendicular feature is not well defined. A similar effect was recently reported for the powder e.s.r. spectrum assigned to $(\text{CN})_4\text{Pt}^{\cdot-}\text{H}_2^-$ radicals.⁸ A broad, weak feature on the high-field side of the central feature due to other radicals could well be the $M_1 = +\frac{1}{2}$ parallel feature. If so, this gives the data listed in the Table. I stress, however, that the maximum value for A_{\parallel} ($^{117/119}\text{Sn}$) is only *ca.* 380 G based on the form of the $-\frac{1}{2}$ feature, and using this value makes no difference to the conclusions drawn below.

At least 11 proton hyperfine features are resolved, and there can be little doubt that these are the central set of the 19 features expected for the $[\text{Me}_3\text{Sn}\cdot\text{SnMe}_3]^+$ cation. These features are very similar to those that we have obtained for the di-silicon cation, and to those published for this⁹ and the di-germanium cation.⁷ As with these cations, these results demonstrate that there is effectively free rotation about the C-Sn bonds, in marked contrast with the di-carbon derivative.¹

If the data in the Table are processed in the usual way,⁹ but using the ($^{117/119}\text{Sn}$) A^0 values of Morton and Preston,¹⁰ approximate orbital populations of 35% 4p and 1% 4s are

TABLE. E.s.r. parameters for various σ -radical cations, $[\text{Me}_3\text{M}\cdot\text{MMe}_3]^+$.

Radical ^a	¹ H Hyperfine coupling/G ^e	g
$(\text{Me}_3\text{C})^{+\text{b,d}}$	32(6H), 4.5(12H)	2.003
$(\text{Me}_3\text{C})^{+\text{e}}$	29 (6H)	—
$(\text{Me}_3\text{C})^{+\text{f}}$	29(6H), 4.2(12H)	—
$(\text{Me}_3\text{Si})^{+\text{g}}$	5.6(18H)	2.0075
f	5.65(18H)	2.0077
h	5.55(18H)	—
$(\text{Me}_3\text{Ge})^{+\text{h}}$	5.39 , 5.18 _⊥ (18H)	$\left\{ \begin{array}{l} 2.0023_{ } \\ 2.0041_{\perp} \end{array} \right.$
$(\text{Me}_3\text{Sn})^{+\text{g}}$	3.4(18H)	$\left\{ \begin{array}{l} 2.0023^{1,1}_{ } \\ 2.110_{\perp} \end{array} \right.$

^a Formed from $\text{Me}_3\text{M}\cdot\text{MMe}_3$ in CFCl_3 except for b. ^b Formed in CCl_4 . ^c $G = 10^{-4}$ T. ^d Ref. 1. ^e Ref. 2. ^f Ref. 3. ^g This work. ^h Ref. 7. ⁱ Assumed: $A(^{117/119}\text{Sn})_{||}$ *ca.* 238 G, \perp 100 ± 2 G. ^j Relative intensities of perpendicular satellite features (averaged over six Q -band spectra) = 17%. The calculated ratio for two equivalent $^{117/119}\text{Sn}$ atoms = 16.35%.

obtained. The latter values are close to the expected spin-polarisation values of 2–4% for unit population and a planar structure.¹¹ The 4p orbital population is also quite reasonable, considering the inaccuracies involved. Thus, if orbital following occurs, as is usually the case,¹² I conclude that the configuration about each tin atom is indeed nearly planar. Since $\text{Me}_3\text{Sn}\cdot$ radicals are strongly pyramidal, as deduced from the large 4s-orbital contribution,¹³ this result is remarkable, and lends support to the postulate that there is near-planar configuration for each central carbon in $[\text{Me}_3\text{C}\cdot\text{CMe}_3]^+$ cations.¹

In our previous work we failed to prepare the $[\text{Me}_3\text{Sn}\cdot\text{SnMe}_3]^-$ σ^* -radical, but we think that $[\text{Ph}_3\text{Sn}\cdot\text{SnPh}_3]^-$ anions were prepared. The huge $^{117/119}\text{Sn}$ coupling constants obtained, showing that the $\text{Ph}_3\text{Sn}\cdot$ units are strongly pyramidal, make a remarkable contrast with those now reported for the σ -cation radicals.

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