The ^1H Nuclear Magnetic Resonance Spectrum of the Stannyl Ion

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Summary The n.m.r. spectrum of a solution of sodium stannyl in liquid ammonia has been obtained and an extremely small $^{119}Sn–H$ coupling constant of 109·4 Hz observed.

Our interest in anionic species of the group IV hydrides prompted us to examine the n.m.r. spectrum of a solution resulting from the stoicheiometric reaction of stannane with sodium in liquid ammonia at −78°. Reactions were carried out as previously described for the GeH_3^- and SiH_3^- ions[1] using standard vacuum line techniques. The hydrogen evolved, measured by means of a Toepler pump, corresponded to reaction (1). The n.m.r. tube was sealed and

$$SnH_4 + Na \rightarrow SnH_3Na + \tfrac{1}{2}H_2 \qquad (1)$$

the spectrum (Figure 1) recorded at −78 °C. Only two sets of resonances are observed, one due to NH_3 and the other due to the SnH_3^- ion. That the sharp resonance at −1·68 p.p.m. does indeed arise from the SnH_3^- ion is confirmed by the observation of satellites arising from coupling to ^{119}Sn and ^{117}Sn and by the fact that subsequent addition of CH_3Cl to this solution produced CH_3SnH_3 (confirmed by i.r. and n.m.r.). Clearly there is no rapid proton exchange occurring with the solvent since the $^{15}N–H$ coupling is clearly visible: the partially collapsed $^{14}NH_3$ spectrum is a consequence of the quadrupole relaxation effect of the ^{14}N nucleus at the low temperature employed to record the spectrum.

The shift of the Sn–H resonance to higher field on removal of the proton from SnH_4 (Table) is expected; the negative charge causing increased shielding, and the chemical shift is in the same region as that for the isoelectronic SbH_3.[3] By analogy with SbH_3 one would expect SnH_3^- to be pyramidal with a ∠ H–Ŝn–H of *ca.* 90°. The change in geometry about the tin nucleus has a dramatic effect on the tin–hydrogen coupling constant (see Table). These changes can be rationalised in terms of the molecular orbital

Table

	δ p.p.m. from ext. TMS	*J* (Hz) $^{119}Sn–H$	*J* (Hz) $^{117}Sn–H$
SnH_3^-	−1·68	109·4	104·9
SnH_4	−3·85	1933	1842
SnH_3^+		2960[2]	
	−7·5	2916	2787

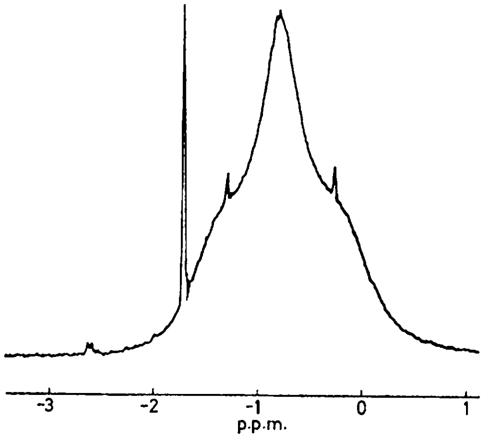

Figure 1. *The* ^1H *n.m.r. spectrum of a solution of* $NaSnH_3$ *in liquid ammonia at* −78°.

diagrams in Figure 2, which have been constructed from the *s* and *p* valence shell orbitals for the three molecules in question. In each case the four lowest lying molecular orbitals are filled. Pople and Santry[4] have shown that the reduced coupling constant is proportional to π [see equation (2)], where the magnitude will depend upon the energy

$$\pi = 4 \sum_{i}^{\text{occ}} \sum_{j}^{\text{unocc}} (\epsilon_i - \epsilon_j)^{-1} C_{sA_i} C_{sB_i} C_{sA_j} C_{sB_j} \qquad (2)$$

separation $(\epsilon_i - \epsilon_j)$ and upon the magnitude of the numerical coefficients C. For the planar SnH_3^+ the $a \rightarrow a^*$ energy is probably not large, making this transition easily accessible. The resulting reduced nuclear spin-spin coupling constant should be positive, and its magnitude will depend upon the coefficients in the above expression. Since a very large value is observed, either these coefficients must be large and/or the energy small. A similar situation pertains in SnH_4 and a large positive reduced coupling constant should be observed. Because SnH_4 has a more "stable" structure (*i.e.* less easily polarisable) than SnH_3^+, the energy of the transition, $a \rightarrow a^*$, is certainly much higher and hence $J(^{119}Sn-^{1}H)$ should be lower for SnH_4 than SnH_3^+, as is observed.

For SnH_3^- two transitions are allowed which can contribute to the coupling between ^{119}Sn and ^{1}H. Both will be readily accessible and like the two previous cases will lead to very large contributions to *J*. However, while the $a \rightarrow a^*$ transition leads to a positive contribution, that for $a' \rightarrow a^*$ will be negative.† The net result is a partial cancellation of two large contributions and a quite small value for $J\ (^{119}Sn-^{1}H)$. The sign of the reduced coupling constant is probably positive, but the sign will depend on the relative energies and coefficients for the transitions involved and could well be negative.

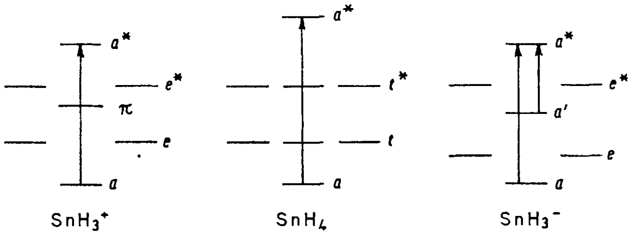

FIGURE 2

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† This has been confirmed by INDO calculations on pyramidal molecules such as NH_3.

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