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High resolution paramagnetic proton resonance spectra of some metal-ethyl compounds

by G. KLOSE

E. B. Baker [1] found, that the indirect spin-spin coupling between the nucleus of the lead isotope ^{207}Pb of leadtetraethyl and the protons of the CH_3 group is bigger than the coupling of the ^{207}Pb isotope with the protons of the CH_2 group attached direct to the metal atom. P. T. Narasimhan and M. T. Rogers obtained the same result for mercury diethyl [2].

We made a study of the spectra of tin tetraethyl and diethyl selenide in order to obtain the different coupling constants and the internal chemical shifts between the protons of the CH_3 and CH_2 groups.

The spectrum of tin tetraethyl of a frequency of 25 Mc/s consists of three intense central lines with several weak satellite lines on either side. These satellite lines are the result of the unequal spin coupling of the ^{117}Sn (spin 1/2, abundance 7,67%) and ^{119}Sn isotopes (spin 1/2, abundance 8,68%) with the CH_3 and CH_2 groups. The observed spectrum is in good agreement with the calculated spectrum (type: $B_3 A_2$, $B_3 A_2 X$, $B_3 A_2 Y$) with the following data:

$$\begin{aligned} J_{\text{H}(\text{CH}_3)\text{—H}(\text{CH}_2)} &= 7,9 \text{ c/s}; \delta = \nu_{\text{H}(\text{CH}_3)} - \nu_{\text{H}(\text{CH}_2)} = -9,3 \text{ c/s}; \\ J_3^{119}\text{Sn—H}(\text{CH}_3) &= 69,6 \text{ c/s}; J_3^{117}\text{Sn—H}(\text{CH}_3) = 66,5 \text{ c/s}; \\ J_2^{119}\text{Sn—H}(\text{CH}_2) &= 51,9 \text{ c/s}; J_2^{117}\text{Sn—H}(\text{CH}_2) = 49,6 \text{ c/s}. \end{aligned}$$

For diethyl selenide we obtained $J_{\text{H}(\text{CH}_3)\text{—H}(\text{CH}_2)} = 7,0 \text{ c/s}$ and $\delta = \nu_{\text{H}(\text{CH}_3)} - \nu_{\text{H}(\text{CH}_2)} = 36,2 \text{ c/s}$. Lines which are the result of a coupling between the ^{77}Se isotope (spin 1/2, abundance 7,5%) and the CH_3 and CH_2 groups were not observed.

The Pauling electronegativities for tin and selenium calculated from the internal chemical shifts confirm the suggestion of Shoolery [2], that the value of the constant in the original Dailey-Shoolery equation [3] must be changed from 1,71 to 2,10 for low electronegativities. A more detailed paper is in preparation.

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 2. NARASIMHAN, P. T., M. T. ROGERS, *J. Am. Chem. Soc.*, 82, 34, 1960.
 3. DAILEY, B. P., J. N. SHOOLERY, *J. Am. Chem. Soc.*, 77, 3977, 1955.
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