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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_3A_2 , $\text{B}_3\text{A}_2\text{X}$, $\text{B}_3\text{A}_2\text{Y}$) with the following data:

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

For diethyl selenide we obtained $J\text{H(CH}_3\text{)}-\text{H(CH}_2\text{)} = 7,0 \text{ c/s}$ and $\delta = \nu_{\text{H(CH}_3\text{)}} - \nu_{\text{H(CH}_2\text{)}} = 36,2 \text{ c/s.}$ 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.