Zeitschrift: Archives des sciences [1948-1980]
Herausgeber: Société de Physique et d'Histoire Naturelle de Genève
Band: 13 (1960)
Heft: 9: Colloque Ampère

Artikel: High resolution paramagnetic proton resonance spectra of some metal-ethyl compounds
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DOI: https://doi.org/10.5169/seals-738632

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

by G. Klose

E. B. Baker [1] found, that the indirect spin-spin coumling 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, B_3A_2X, B_3A_2Y) with the following data:

$J\,H(CH_3)—H(CH_2) = 7{,}9$ c/s; $\delta = \nu_{H(CH_3)}—\nu_{H(CH_2)} = —9{,}3$ c/s;
$J_3\,^{119}Sn—H(CH_3) = 69{,}6$ c/s; $J_3\,^{117}Sn—H(CH_3) = 66{,}5$ c/s;
$J_2\,^{119}Sn—H(CH_2) = 51{,}9$ c/s; $J_2\,^{117}Sn—H(CH_2) = 49{,}6$ c/s.

For diethyl selenide we obtained $J\,H\,(CH_3) — H\,(CH_2) = 7{,}0$ c/s and $\delta = \nu_{H(CH_3)}—\nu_{H(CH_2)} = 36{,}2$ 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 elecctronegativities. 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.