63. On the Relation between One-Bond Coupling Constants and the s-Electron Density at the Nucleus

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Summary

A comparison of *Mössbauer* isomer shifts and direct Sn, Sn-coupling constants for a series of di- and polytin compounds indicates that the s-electron density at the Sn-atom has little influence on this coupling.

The publication of a paper by *Kunz* [1] in which he discusses the relative importance of the s-electron density at the nucleus $\psi^2_{ns}(0)$ and the mutual polarizability $\pi(A, B)$ in determining the magnitude of direct element-element NMR. coupling constants prompts us to communicate the results of some recent investigations on organotin compounds which support his conclusion that the latter term is the dominant one.

We had previously observed [2] that the direct Sn, Sn-coupling constant in a series of hexaalkylditins correlates well with the sum of the *Taft* σ^*-values for the six alkyl groups, but not with the E_s-values for these groups. We have now carried out *Mössbauer* measurements on a series of organotin compounds $R_n Sn(SnMe_3)_{4-n}$ ($n=0-3$) and on $Me_4 Sn_2 (OAc)_2$ in which the Sn, Sn-coupling constant varies between 14980 and 867 Hz (the relevant NMR. data have been published previously [2] [3] with one exception).

The *Mössbauer* isomer shift directly reflects the s-electron density at the nucleus, and is thus a useful tool in assessing the importance of this parameter in influencing Sn-element coupling constants. It does however have the disadvantage that the natural line width limits its sensitivity: thus for example although the Sn-chemical

Table. *Sn, Sn-Coupling Constants and* Mössbauer *Parameters for Di- and Polytin Compounds*

Compound	$^1J(^{119}Sn, ^{119}Sn)$ (Hz)	Isomer Shift S (mm/s)	Line Width Γ (mm/s)
$Me_4Sn_2(OAc)_2$	14980	1.44[a]	0.70
$Me_3SnSnMe_3$	4404	1.32	0.68
$Me_2Sn(SnMe_3)_2$	2873	1.35	0.65
$BuSn(SnMe_3)_3$	1548	1.38	0.66
$Sn(SnMe_3)_4$	876	1.36	0.71

[a]) Quadrupole splitting 3.53 mm/s. Accuracy of parameters: $J \pm 6$ Hz, $S \pm 0.04$ mm/s, $\Gamma \pm 0.07$ mm/s.

shifts of the non-equivalent nuclei in $Sn(SnMe_3)_4$ differ by *ca.* 700 ppm, the *Mössbauer* spectrum consists of only one line (as does that of $Sn(SnPh_3)_4$ [4]).

The relevant experimental data are contained in the *Table;* for reference, the isomer shift of tetramethyltin is 1.16 mm/s, that of metallic tin 2.5 mm/s [5]. The relatively high *S*-value for $Me_4Sn_2(OAc)_2$ is explained by the fact that the Sn-atoms are pentacoordinate, the structure being formally of the type given in the formula, though in fact the CH_3CO_2 ligand is isobidentate [3]. The Sn, Sn-bond in compounds of this type is known to be considerably shorter than in simple ditins where tin has the coordination number four [6] [7].
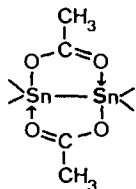
Thus if we neglect this molecule, the remaining isomer shifts lie very close together, and indicate that the electron density at the Sn-nucleus increases by about 5% on going from Me_6Sn_2 to $Me_{12}Sn_5$, although the Sn, Sn-coupling constant decreases by a factor of about 5 ($^1J(Sn, C)$ in the Me_3Sn groups is almost constant in this series at 240 ± 4 Hz). It thus appears quite clear that fluctuations of $\psi^2_{5s}(0)$ are not involved in determining the one-bond coupling constant $^1J(Sn, Sn)$ for compounds in which the Sn-atom has a constant coordination number. In conjunction with *Kunz's* results [1], it seems that a generalization of this statement to include other couplings involving main group elements is justified.

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