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Preliminary communication

NMR ^1J(Sn—Sn) COUPLING CONSTANTS IN HEXAORGANODITINS

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Summary

Direct one-bond tin—tin coupling constants have been measured in a series of hexaorganoditins; the magnitude of the coupling shows a marked dependence on the effective nuclear charge on tin.

During an investigation of the ^{13}C-NMR spectra of organotin compounds [1], three hexaorganoditins were studied. While the spectra showed a large variation in ^2J(C—Sn—Sn), ^1J(C—Sn) was almost invariant. This Preliminary communication describes the results of ^{119}Sn-NMR investigations made on a series of ditins. The data obtained are given in Table 1. Previously only Me_6Sn_2 had been studied in detail [2] and for this $^1J(^{119}\text{Sn}—^{117}\text{Sn})$ was found to be +4264 Hz. The value found in the present work was 4211 ± 6 Hz.*

Table 1 shows that very large variations are observed in ^1J(Sn—Sn) when different alkyl groups are bonded to tin. The trends in compounds I to X can be rationalised in terms of the number of protons bound to the carbon atoms α to tin. Increased alkyl substitution at these carbon atoms causes a rapid decrease in ^1J(Sn—Sn). The reason is apparently that the (+*I*) inductive effect or electron-releasing ability of the alkyl groups bound to tin is increased, and therefore the effective nuclear charge on tin lowered: ^1J(Sn—Sn) shows a linear correlation with the sum of the Taft constants of the six alkyl groups. Similar, though smaller, changes have been observed for $^1J(^{119}\text{Sn}—^{77}\text{Se})$ in organotin selenides [3] and for $^1J(^{119}\text{Sn}—\text{H})$ in organotin hydrides. In the latter case, no convincing explanation has previously been offered for the variations [4].

Compounds XI to XIII show a similar trend to that already discussed for hexaalkylditins, a decrease in ^1J(Sn—Sn) occurring on alkyl substitution

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* The spectra were recorded in the PFT-mode with proton noise decoupling using a Bruker HFX-10 spectrometer, operating at 33.546 MHz and 2.1T and coupled to a Nicolet Series 1080 computer; they normally consisted of 4K data points corresponding to a sweep width of 12500 Hz, giving a digital resolution of ca. 3 Hz.

TABLE 1

CHEMICAL SHIFTS AND COUPLING CONSTANTS IN HEXAORGANODITINS

Compound	$R_3Sn—SnR'_3$		$\delta(R_3Sn)$ (ppm)[a]	$\delta(R'_3Sn)$	$^1J(^{119}Sn—^{117}Sn)$ (Hz)
	R	R′			
I	Me	Me	−108.7		4211
II	Me	Et	−108.1	−61.8	3342
III	Me	s-Bu	−105.3	−45.3	2686
IV	Me	C_6H_{11}	−103.8	−78.3	2716
V	Et	Et	−59.9		2583
VI	Et	n-Bu	−65.7	−79.7	2570
VII	i-Pr	i-Pr	−29.1		1155
VIII	n-Bu	n-Bu	−83.2		2625
IX	i-Bu	C_6H_{11}	−93.2	−85.2	2422
X	b	b	−21.5		730
XI	Me	Ph	−91.5	−150.6	4075
XII	Et	Ph	−48.7	−140.4	3014
XIII	i-Bu	Ph	−86.8	−146.9	3058

[a] δ(internal Me_4Sn) = 0; negative sign indicates high-field shift. C_6D_6 was used as internal lock, and solids were dissolved in $CHCl_3$. [b] R_3 = R'_3 = i-Pr_2, t-Bu.

of the methyl groups in $Me_3SnSnPh_3$. No correlation of $^1J(Sn—Sn)$ with Taft constants is possible in this case, however, presumably because interaction between the aromatic π-system and empty tin d orbitals causes changes in hybridisation or effective nuclear charge.

These results indicate that the effective nuclear charge on tin may well play a more important role in determining the size of coupling constants in organotin compounds than has previously been realised. The relation between coupling constant and s-character, first proposed in 1961 [5] and since modified [6] was criticized as early as 1965 [7] on the grounds that it ignores the effect of effective nuclear charge. Though rehybridisation at the tin atom must apparently be postulated in order to explain the values of $^1J(Sn—C)$ and $^2J(Sn—H)$ in 5- and 6-coordinated organotin compounds, changes in effective nuclear charge may be mainly responsible for changes in these coupling constants in 4-coordinated compounds (and indeed for changes in coupling constants in organic compounds of metals in general). We intend to use compounds of the type $R_3Sn—MR_3$ (M = C, Si, Pb) as model compounds to study the effect of changes in R on $^1J(Sn—M)$ and $^1J(Sn—C_{alkyl})$.

The PFT technique also lends itself readily to the study of other tin—tin coupling constants $^{n+1}J(Sn—X_n—Sn)$, where X is either tin or a "heteroatom" e.g. C, O, S. It has been found , for example, that in Et_3SnSn-i-Bu_2SnEt_3 $^2J(Sn—Sn)$ is 430 Hz, in $Et_3Sn(CH_2)_2SnEt_3$ $^3J(Sn—Sn)$ is 879 Hz, and in $(ClBu_2Sn)_2O$ $^2J(Sn—O—Sn)$ is 72 Hz.

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