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Dependence of $|^1J(^{119}Sn^{13}C)|$ on the C–Sn–C Angle in n-Butyltin(IV) Compounds

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In recent years there has been an increase in the application of ^1H, ^{13}C and ^{119}Sn NMR parameters for the characterization of the composition and coordination sphere geometry of organotin(IV) compounds and their complexes. There were also attempts to use some of these parameters for a qualitative or a quantitative characterization of the structure of these compounds. The most important dependences reported in refs. 1 and 2 describe the relationships between coupling constants $|^1J(^{119}Sn^{13}C)|$ or $|^2J(^{119}Sn^1H)|$, respectively, and the C–Sn–C bond angle (θ) in methyltin(IV) compounds. Lockhart *et al.* [1] found a simple linear correlation between coupling constants $|^2J(^{119}Sn\text{-}^{13}C)|$ of a group of tetra-, penta- and hexacoordinated methyltin(IV) compounds, studied by solid state ^{13}C NMR spectroscopy, and their bond angles θ, determined by X-ray diffraction, in the form:

$$|^1J(^{119}Sn^{13}C)| = 11.4\theta - 875 \; (r = 0.995; n = 9) \qquad (1)$$

From the comparison of coupling constants $|^1J(^{119}Sn^{13}C)|$ and $|^2J(^{119}Sn^1H)|$ of hexacoordinated dialkyltin chelate complexes in $CDCl_3$ solutions with angles θ obtained from X-ray analysis of corresponding crystals, Howard *et al.* [2] derived the linear relationships:

$$\theta = 2.28|^2J(^{119}Sn^1H)| - 46.4 \qquad (r = 0.978; n = 7) \qquad (2)$$

$$\theta = 0.178|^1J(^{119}Sn^{13}C)| + 14.74 \quad (r = 0.94; \; n = 5) \qquad (3)$$

Recently, we have reported [3] the results of a detailed study of n-butyltin(IV) compounds and their complexes. We present here a revealed linear dependence of $|^1J(^{119}Sn^{13}C)|$ in tetra-, penta- and hexacoordinated n-butyltin(IV) compounds measured in $CDCl_3$ solutions on the C–Sn–C angles θ obtained from X-ray analysis.

$$|^1J(^{119}Sn^{13}C)| = (9.99 \pm 0.73)\theta - (746 \pm 100) \qquad (4)$$
$$(r = 0.982; n = 9)$$

A plot of $|^1J(^{119}Sn^{13}C)|$ against θ is shown in Fig. 1, where experimental data are shown by points with numbers corresponding to those given to the compounds in Table I. The full line corresponds to the derived eqn. (4), while dashed lines correspond to eqns. (1) and (3), respectively.

As seen from Fig. 1, the experimental points are situated near to the statistically obtained eqn. (4) which is not very different from eqn. (1). Only the points **5** and **10** reveal larger deviations from the derived relationship. In the case of compound **5** this deviation is caused by an 'unnatural' value of

TABLE I. Crystallographic and Solution NMR Data for n-Butyltin(IV) Compounds

Compound[a]	Coordination number	Solution NMR data		Crystallographic data	
		$\lvert ^1J(^{119}Sn^{13}C)\rvert$ (Hz)	Reference	θ (°)	Reference
1 Bu_4Sn	4	307	2	109.5[b]	
2 $Bu_2Sn(SC_5H_3\text{-}5\text{-}NO_2)_2$	4(6)	522.5	4	129.2	5
3 $Bu_3SnCl_2^-$	5	494.2	this work[c,d]	119.8[e,f]	6
4 Bu_2SnX	5	614	7	132.5[f]	8
5 $Bu_2SnCl_2 \cdot dppoe$	5	598.2	this work[c]	154.3	9
6 $(Bu_2SnOC(O)CCl_3)_2O$	5	696.0	this work[c]	143	10
		646.3	this work[c]	137	10
7 $Bu_2Sn(OCH_2CH_2O)$	5(6)	653	11	138.6	12
8 $Bu_2Sn(morf \cdot dtc)_2$	6	600.2	this work[c]	141	13
9 $Bu_2SnCl_2 \cdot phen$	6	1016	2	177	14
10 $Bu_2Sn(dbzm)_2$	6	880	2	180	2

[a] Abbreviations: Bu = n-butyl, Ph = phenyl, X = 4,6-O-benzylidene-α-D-glucopyranoside, morf•dtc = $O(CH_2CH_2)_2NC(S)S$, dppoe = $Ph_2P(O)CH_2CH_2P(O)Ph_2$, phen = 1,10-phenanthroline, dbzm = dibenzoylmethane. [b] Tetrahedral geometry assumed. [c] See also ref. 3. [d] Cation $[Bu_4N]^+$. [e] Cation $[Ph_3PCH_2Ph]^+$. [f] Average value.

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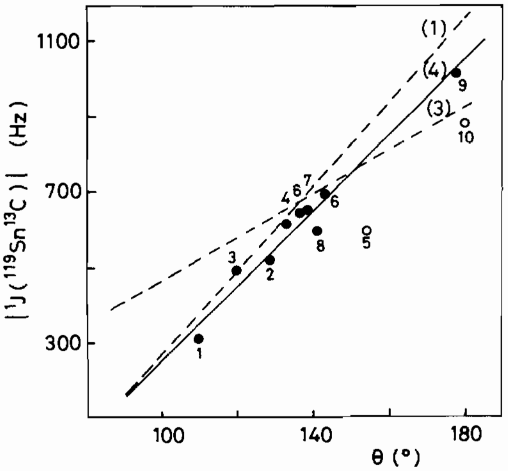

Fig. 1. Plot of $|^1J(^{119}Sn^{13}C)|$ *vs.* C–Sn–C bond angle θ for n-butyl- and methyltin(IV) compounds. Compound numbers correspond to those given in Table I. Full line – this work, dashed line – refs. 1 and 2 (see text).

$|^1J(^{119}Sn^{13}C)|$ which reveals a fast exchange between Bu_2SnCl_2 and its complex with dppoe on the NMR time scale. This explanation is supported by the value of $\delta(^{119}Sn) = -66.6$ pm for compound **5**, which is typical of compounds with the coordination number of Sn between four and five [3] and also by the presence of one signal only in ^{31}P NMR spectra instead of two signals expected according to the results of X-ray analysis [9]. In the case of compound **10** the deviation could be explained by a large change in θ values during the transition of compound **10** from the solid state into solution. A similar change to that mentioned above was revealed for the compound $Me_2Sn(acac)_2$ [1, 2]. Therefore, the data for compounds **5** and **10** were not used for the calculation of eqn. (4). A similarity of the relations (1) and (4) is supported by nearly identical values of coupling constants $|^1J(^{119}Sn^{13}C)|$ calculated for the angle $\theta = 90°$ (151 Hz and 153 Hz, respectively). According to Lockhart *et al.* [1] these values correspond to the contribution of the orbital and dipolar terms to $|^1J(^{119}Sn^{13}C)|$. The value of $|^1J(^{119}Sn^{13}C)|$ for $\theta = 90°$ calculated from relation (3) is substantially higher (~423 Hz) than the values given above.

We assume that a large difference between relations (1) and (4) with respect to (3) is due to an inadequate and insufficient choice of data used for the calculation of eqn. (3).

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