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FOURIER TRANSFORM NMR INVESTIGATIONS ON ORGANOTIN COMPOUNDS

V *. COUPLING CONSTANTS AND CHEMICAL SHIFTS IN SIMPLE TETRAORGANOTINS

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Summary

Carbon-13 NMR data are reported and discussed for 32 simple tetraorganotins $R_nSnR'_{4-n}$ (n = 0—4) in which the tin atom is four-coordinate. It is found that the value of ^1J(Sn—C) in compounds R_4Sn depends on the effective nuclear charge at tin; in mixed organotins Bent's postulate is apparently verified, and in a number of cases coupling constants can again be correlated with Taft σ^* constants for the alkyl groups. The values of $^1J(Sn—\underline{C}H_2)$ in benzyltin compounds are clearly anomalous. Long-range tin—carbon coupling constants are discussed. The chemical shifts of the carbons in methyl groups bound to tin provide a second useful probe for estimating the electron-withdrawing or electron-releasing power of alkyl and other groups bound to the tin atom.

Introduction

Though the main factors affecting ^{13}C chemical shifts and coupling constants are well established, and though many classes of organic compounds have been studied in some detail [2], relatively little detailed investigations on organometallic compounds have been carried out. Our interest in the chemistry of the elements of Group IVB has recently prompted us to begin a ^{13}C NMR study of organotin compounds [1]. Underlying trends can most readily be observed when closely related compounds are compared, and we therefore thought it necessary to investigate a number of simple tetraorganotins of the type $R_nSnR'_{4-n}$, in which the tin atom has a coordination number of four. Organotin compounds have the advantage over the other Group IVB elements E (except lead) that the

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* For parts I—IV see ref. 1.

TABLE 1

CARBON-13 CHEMICAL SHIFT DATA FOR COMPOUNDS OF THE TYPE $R_nSnR'_{4-n}$ (in ppm; δ(TMS) = 0)

Bz = CH_2Ph; Vi = $CH{=}CH_2$

Compound	R	n	R'	δ(C_1)	δ(C_2)	δ(C_3)	δ(C_4)	δ($C_{1'}$)	δ($C_{2'}$)	δ($C_{3'}$)	δ($C_{4'}$)
I [a]	Me	4		−9.6							
II [a]	Et	4		0.0	11.1						
III [a]	Pr	4		12.3	20.9	19.2					
IV	i-Pr	4		14.3	22.6						
V [a]	Bu	4		9.1	29.6	27.6	13.7				
VI	s-Bu	4		23.4	18.6/ 29.6	14.5					
VII	Bz	4		19.0	141.6	128.6	128.4				
VIII	$PhCH_2CH_2$	4		11.1	32.8	145.3	128.4				
IX [b]	Me	3	Et	−11.0				2.8	10.7		
X [b]	Me	3	Pr	−10.4				13.9	20.5	18.7	
XI	Me	3	i-Pr	−12.0				13.7	21.2		
XII [b]	Me	3	Bu	−10.5				11.1	29.2	27.3	13.8
XIII	Me	3	i-Bu	−9.6				23.2	27.2	26.5	
XIV	Me	3	t-Bu	−12.1				21.1	29.9		
XV	Me	3	Bz	−10.3				20.1	142.7	128.4	128.4
XVI	Me	3	$PhCH_2CH_2$	−10.4				12.6	32.7	144.8	128.3
XVII [c]	Me	3	$C{\equiv}CC_3H_7$	−8.1				81.7	104.6	22.7	22.3
XVIII [d]	Me	3	$C{\equiv}CC_4H_9$	−8.1				81.4	110.4	19.9	31.4
XIX	Me	3	$C{\equiv}CSnMe_3$	−7.9				116.1	116.1		
XX	Et	3	t-Bu	−0.5	11.3			24.1	31.0		
XXI	Et	3	$CH{=}CHPh$	1.1	11.2			127.7	139.2	147.3	128.6
XXII	Et	3	$C{\equiv}CPh$	2.6	11.1			83.3	97.8	132.3	128.4
XXIII	Pr	3	t-Bu	11.3	20.9	19.4		23.4	30.9		
XXIV	i-Pr	3	t-Bu	14.7	22.6			27.5	31.8		
XXV	Bu	3	t-Bu	8.1	29.7	27.9	13.7	23.5	30.9		
XXVI	Vi	3	t-Bu	138.0	138.0			26.0	30.4		
XXVII	Me	2	Bu	−11.5				10.4	29.4	27.4	13.8
XXVIII	Me	1	Et	−14.4				0.9	11.0		
XXIX	Me	1	Pr	−12.6				12.8	20.7	19.0	
XXX	Me	1	i-Pr	−16.8				13.7	22.2		
XXXI	Me	1	Bu	−12.7				9.7	29.6	27.6	13.9
XXXII	Me	1	Ph	−10.6				139.2	128.5	128.9	136.8

[a] Data from ref. 1a. [b] Data from ref. 1d. [c] δ($C_{5'}$) 13.5 ppm. [d] δ($C_{5'}$) 22.1, δ($C_{6'}$) 13.7 ppm.

abundance of magnetic isotopes (^{119}Sn, 8.68% and ^{117}Sn, 7.67%) is such as to allow ready determination of the coupling constants ^nJ(E—C); the values of these provide information on the electronic structure of the organotins which should be more reliable than that obtained from ^nJ(Sn—H) values.

Experimental

Spectra were recorded in the pulse Fourier transform mode with proton noise decoupling using a Bruker-Physik HFX 90 spectrometer operating at a resonance frequency of 22.63 MHz in conjunction with a Nicolet Series 1080 computer (16K data points) for data accumulation and processing. The digital resolution of 0.76 Hz (sweep width 6250 Hz) gives a coupling constant accuracy of ±0.8 Hz and a chemical shift accuracy of 0.03 ppm. The samples (10 mm sample tube) were, unless otherwise stated, neat liquids containing ca. 5% hexadeuterobenzene as internal lock and ca. 2% TMS as internal standard. Solid samples were dissolved in $CDCl_3$, which then served as internal lock.

A majority of the compounds studied are described in the literature; the data on a number of them have already been reported [1] and are included here for purposes of comparison. Unless otherwise stated, they were prepared by treating $SnCl_4$ or organotin halides with the appropriate Grignard reagent:

$$R_nSnX_{4-n} + (4\text{-}n)R'MgX' \rightarrow R_nSnR'_{4-n} + (4\text{-}n)MgXX' \qquad (1)$$

(X = Cl, Br; n = 0—4)

Compounds of the type $R_3SnC{\equiv}CR'$ (R′ = alkyl, phenyl) were obtained by treating the corresponding diethylaminotin R_3SnNEt_2 with the acetylene $R'C{\equiv}CH$ (molar ratio 1 : 1); a slightly exothermic reaction occurred on mixing. The reactants were heated at 80°C for 1 h, diethylamine removed at the water pump, and the resulting oils distilled as colourless liquids.

Bis(trimethylstannyl)acetylene was precipitated as a colourless crystalline solid (m.p. 54—58°C; lit. [3] 55—59°C) when a stream of dry acetylene gas was passed into neat trimethyldiethylaminotin. Removal of diethylamine at the water pump left pure $Me_3SnC{\equiv}CSnMe_3$ in 98% yield. Raman: ν_{max}(C≡C) 2070 cm^{-1}; ^{1}H NMR: δ(C$\underline{H}_3$) 0.30, ^2J(Sn—H) 60.3 Hz.

trans-β-Triethylstannylstyrene was prepared from phenylacetylene and triethyltin hydride as described in the literature [4].

Results and discussion

The data obtained are presented in Tables 1 and 2; the normal sign convention is used for chemical shifts. Coupling constants and chemical shifts will be discussed separately.

(a) Coupling constant data

It is generally accepted that the Fermi contact interaction is the main factor which determines the value of tin—carbon coupling constants. According to the Pople—Santry treatment, [5] modified by making the average-energy approxi-

TABLE 2

TIN—CARBON COUPLING CONSTANT DATA FOR COMPOUNDS OF THE TYPE $R_nSnR'_{4-n}$ (^nJ in Hz)

Compound	R	n	R′	^1J(Sn—C)	^2J(Sn—C)	^3J(Sn—C)	^1J(Sn—C′)	^2J(Sn—C′)	^3J(Sn—C′)
I [a]	Me	4		338.0					
II [a]	Et	4		321.0	23.0				
III [a]	Pr	4		314.0	21.0	51.0			
IV	i-Pr	4		301.0	15.0				
V [a]	Bu	4		314.0	20.0	52.0			
VI	s-Bu	4		300.0	15/c	39.6			
VII	Bz	4		257.9	c	c			
VIII	$PhCH_2CH_2$	4		309.8	18.3	23.0			
IX [b]	Me	3	Et	319.0			373.0	24.0	
X [b]	Me	3	Pr	319.0			369.0	21.0	56.0
XI	Me	3	i-Pr	305.2			409.0	12.9	
XII [b]	Me	3	Bu	319.0			368.0	21.0	53.0
XIII	Me	3	i-Bu	318.1			367.0	21.0	c
XIV	Me	3	t-Bu	295.3			437.0	0.0	
XV	Me	3	Bz	326.5			296.0	39.6	c
XVI	Me	3	$PhCH_2CH_2$	321.4			358.6	18.2	c
XVII	Me	3	$C{\equiv}CC_3H_7$	404.3			c	c	c
XVIII	Me	3	$C{\equiv}CC_4H_9$	404.3			506.6	105.2	c
XIX	Me	3	$C{\equiv}CSnMe_3$	399.8			c	c	
XX	Et	3	t-Bu	294.4	23.7		378.0	0.0	
XXI	Et	3	CH=CHPh	349.5	24.4		387.6	64.1	c
XXII	Et	3	C≡CPh	387.6	23.5		c	c	c
XXIII	Pr	3	t-Bu	288.5	20.5	d	378.0	0.0	
XXV	Bu	3	t-Bu	291.0	c	c	c	0.0	
XXVI	Vi	3	t-Bu	435.5	d		469.0	0.0	
XXVII	Me	2	Bu	302.1			348.7	20.6	54.1
XXVIII	Me	1	Et	287.7			337.2	23.7	
XXIX	Me	1	Pr	285.3			329.6	20.6	51.9
XXX	Me	1	i-Pr	248.7			338.8	15.3	
XXXI	Me	1	Bu	286.1			330.3	19.9	53.5
XXXII	Me	1	Ph	374.6			511.0	c	51.0

[a] ± 1.5 Hz, values in good agreement with ref. 12. [b] Values from ref. 1d. [c] Not determined. [d] Not observed.

mation, J(Sn—C) is given by the following equation:

$$J(\mathrm{Sn{-}C}) = \frac{64\beta^2 h}{9} \cdot \gamma_{\mathrm{Sn}}\gamma_{\mathrm{C}} \cdot \alpha^2{}_{\mathrm{Sn}}\alpha^2{}_{\mathrm{C}} \cdot \psi^2_{5s(\mathrm{Sn})}(\mathrm{O}) \cdot \psi^2_{2s(\mathrm{C})}(\mathrm{O}) \cdot (\Delta E)^{-1}$$

Here α^2 is the *s*-character of the hybrid orbital used to form the Sn—C bond and ΔE is an average excitation energy; γ is the magnetogyric ratio of the nucleus concerned, $\psi^2_{ns}(\mathrm{O})$ is the valence *s*-electron density at the nucleus.

Although it seems likely that the average-energy approximation is valid for simple tetraalkyltins, it may well not hold for systems where the tin atom is bonded to an *sp* or sp^2 carbon atom.

(i) Compounds of the type R_4Sn. In compounds I—VI, regression analysis shows that a very close correlation ($r = 0.995$) is found between ^1J(Sn—C) and the sum of the Taft σ^* constants of the four alkyl groups. (Only the magnitude of r is given here and subsequently; r-values are collected in Table 3). This linear relation suggests that, since α^2 remains constant (in each case the tin atom must be sp^3-hybridised), the effective nuclear charge Z at tin plays a very important role in determining ^1J(Sn—C); Grant and Litchman [6] have earlier suggested that Z is a dominant factor contributing to ^1J(C—H) in substituted methanes. The regression analysis allows us to estimate ^1J(Sn—C) for the as yet unprepared tetrakis(t-butyl)tin: the value is 280 Hz. It also allows us to calculate σ^* for the β-phenylethyl group; the value of —0.15 so obtained differs somewhat from Taft's [7] value, +0.08. The value of ^1J(Sn—C) for tetrabenzyltin (VII), 257.9 Hz, is clearly anomalous, being of the same approximate magnitude as ^1J(Sn—C) in a hexaalkylditin $R_3SnSnR'_3$. It is known from electron-diffraction (Me_4Sn [8]) and X-ray measurements ($(PhCH_2)_4Sn$ [9]) that the Sn—C bond length in both compounds is (within experimental error) the same, 2.18 Å, and that the angle C—Sn—C is in both cases the tetrahedral angle; other factors must therefore be involved in determining the large difference in ^1J. We shall return to this point below.

(ii) Compounds of the type Me_3SnR. Considering compounds I and IX—XIV, the correlation coefficient for the relation between $^1J(\mathrm{Sn{-}CH_3})$ and $\sigma^*(R)$ is

TABLE 3

CORRELATION COEFFICIENTS |r| DETERMINED FROM REGRESSION ANALYSES

Compounds	Relation between A and B		|r|	n [a]
	A	B		
I—VI	^1J(Sn—C)	$\Sigma\sigma^*$(R)	0.995	6
I, IX—XIV	$^1J(\mathrm{Sn{-}CH_3})$	σ^*(R)	0.982	7
I, IX—XIV	^1J(Sn—C')	σ^*(R)	0.977	7
I, XXVIII—XXXII	$^1J(\mathrm{Sn{-}CH_3})$	$\Sigma\sigma^*(R_3)$	0.996	6
I, XXVIII—XXXII	^1J(Sn—C')	$\Sigma\sigma^*(R_3)$	0.035	6
I, XXVIII—XXXII	$\Sigma\ ^1J$	$\Sigma\sigma^*$	0.911	6
I, V, XII, XXVII, XXXI	$\Sigma\ ^1J$	$\Sigma\sigma^*$	0.999	5
I, IX—XVII, XXVII—XXXII	$^2J(\mathrm{Sn{-}CH_3})$	$^1J(\mathrm{Sn{-}CH_3})$	0.954	17
I—VI	α-effect	σ^*	0.961	6
XIV, XX, XXIII—XXV	$\delta(C_{1'})$	$\Sigma\sigma^*(R_3)$	0.976	5
XIV, XX, XXIII—XXV	$\delta(C_{2'})$	$\Sigma\sigma^*(R_3)$	0.981	5

[a] Number of compounds.

0.982. For the same compounds, r for the relation between $^1J(\mathrm{Sn{-}C'})$ and $\sigma^*(R)$ is 0.977. The value of $^1J(\mathrm{Sn{-}CH_2Ph})$ in compound XV is again very low; however, in each compound one observes a decrease in $^1J(\mathrm{Sn{-}C})$ and an increase in $^1J(\mathrm{Sn{-}C'})$ compared with the values in Me_4Sn and R_4Sn. This trend is the one expected when the theory of isovalent hybridisation, as postulated by Bent [10], is applied. A simple model would suggest that the percentage increase in $^1J(\mathrm{Sn{-}C'})$ (compared to R_4Sn) should be three times the percentage decrease in $^1J(\mathrm{Sn{-}C})$ (compared to Me_4Sn): for R = Et, Pr, Bu this is true to within ca. 1%, for R = i-Pr to within 4%, while for Me_3Sn-t-Bu the deviation (using the estimated value of 280 Hz for t-Bu_4Sn) is ca. 10%. These differences may well be due to changes in the interbond angles at tin caused by increasing chain branching in R. For compounds I and IX—XIV there is no good correlation of Σ^1J with $\Sigma\sigma^*$.

According to Bent's hypothesis, replacement of a methyl group in Me_4Sn by an electron-withdrawing residue should cause an increase in $^1J(\mathrm{Sn{-}\underline{C}H_3})$; this is clearly shown in the alkynyltins XVII—XIX. No J values for the tetraalkynyltins have as yet been measured, and the absence of the Nuclear Overhauser Effect (NOE) made measurement of $^1J(\mathrm{Sn{-}C'})$ difficult, so that an accurate value was obtained only for compound XVIII; from this and the $^1J(\mathrm{Sn{-}\underline{C}H_3})$ value one can calculate an approximate value for $^1J(\mathrm{Sn{-}C})$ in $(RC{\equiv}C)_4Sn$ of 700 Hz. Similarly, using the data from $Et_3SnCH{=}CHPh$ (XXI) one can calculate an approximate value for $(RCH{=}CH)_4Sn$ of 500 Hz, which compares well with the literature value [11] of 519 Hz for tetravinyltin.

(iii) Compounds of the type t-BuSnR$_3$ (XIV, XX, XXIII, XXV, XXVI). The values of $^1J(\mathrm{Sn{-}C})$ are those expected from the arguments presented above, though the variations are surprisingly small, particularly between compound XIV and the remaining compounds. Determination of $^1J(\mathrm{Sn{-}C'})$, the coupling between tin and the quaternary carbon, was again made difficult by the low signal intensity, caused by the absence of the NOE and probably by a relatively long T_1 for this carbon; it was necessary to add chromium tris(acetylacetonate) to eliminate the NOE for the other carbons and thus increase the number of FID accumulations possible before the computer memory was filled. Line overlapping also prevented determination of $^1J(\mathrm{Sn{-}C'})$ for compound XXV, and no satisfactory coupling constant data were obtained for compound XXIV. The limited data available do however indicate a trend not observed in the Me_3SnR series, namely that a decrease in $^1J(\mathrm{Sn{-}C'})$ is accompanied by a decrease in $^1J(\mathrm{Sn{-}C})$; this parallels the behaviour observed in hexaalkylditins [1,12], where a large decrease in $^1J(\mathrm{Sn{-}Sn})$ is accompanied by a small decrease in $^1J(\mathrm{Sn{-}C})$.

(iv) Compounds of the type Me$_n$SnBu$_{4-n}$ (I, V, XII, XXVII, XXXI). $^1J(\mathrm{Sn{-}C})$ decreases steadily on going from Me_4Sn (338 Hz) to $MeSnBu_3$ (286 Hz); it similarly decreases on going from Me_3SnBu (368 Hz) to Bu_4Sn (310 Hz). The correlation coefficient for the relation between Σ^1J and $\Sigma\sigma^*$ is 0.999. For compounds XII, XXVII and XXXI, $^1J(\mathrm{Sn{-}C'})$ is ca. 15% larger than $^1J(\mathrm{Sn{-}C})$, as Bent's hypothesis requires. Thus in a series of very closely related compounds such as this, the values of ^1J can be explained on the basis of Z and of Bent's postulate. Deviations from tetrahedral bond geometry at tin would appear to be only very small.

(v) Long-range coupling constants. In the compounds reported on here, $^2J(\text{Sn—C})$ varies from 0.0 to 105.2 Hz. The variation is particularly striking when primary, secondary and tertiary alkyl groups are considered e.g. compounds IX, XI and XIV. The value in a secondary alkyl group is ca. 50% of that in a primary group, while in the t-butyl group the value is zero; in the same three compounds, $^1J(\text{Sn—C}')$ increases steadily. ^2J in the benzyl group is however larger than in the ethyl group. At this stage, a rationalisation of the values does not appear possible.

When ^2J is compared for the three closely related groups CH_2CH_2Ph, $CH{=}CHPh$ and $C{\equiv}CPh$, an increase from 18.2 via 64.1 to 105.2 Hz is observed; in the same series (XVI, XXI, XXII) $^1J(\text{Sn—C}')$ increases from 358.6 to 506.6 Hz. The variations in ^2J are in this case obviously related to the changes in bond hybridisation (and therefore bond geometry); a simple correlation with the interbond angle $\angle$SnCC is however not found. There is also no correlation with the values of $^2J(\text{CH})$ in ethane, ethylene and acetylene; the literature values [13] for these couplings are —4.5, —2.4 and +49.4 Hz respectively.

(vii) Relation between $^2J(\text{Sn—C}\underline{\text{H}}_3)$ and $^1J(\text{Sn—}\underline{\text{C}}\text{H}_3)$ in methyltin compounds. McFarlane [14] has shown that, for a limited number of methyltin compounds, an approximately linear relation is found between $^2J(\text{Sn—C}\underline{\text{H}}_3)$ and $^1J(\text{Sn—}\underline{\text{C}}\text{H}_3)$, though the straight line obtained when these couplings are plotted against each other does not go through the origin. We have been able to confirm his findings for a much larger number of compounds in the tetraorganotin series: the correlation coefficient for a total of seventeen compounds Me_nSnR_{4-n} (taken from those discussed here) is 0.954. The few data on $^nJ(\text{Sn—H})$ in higher alkyltin compounds which are to be found in the literature indicate that there is no simple relation between $^nJ(\text{Sn—C})$ and $^{n+1}J(\text{Sn—H})$ for such compounds; further studies are however required to clarify the situation.

(b) Chemical shift data

It is now well-established that there is a direct correlation between $\delta(\text{C})$ and the net charge on the carbon atoms in the paraffin series [15]. The carbon chemical shifts in tetraalkyltins can similarly be used as a probe for estimating electron density distribution: we have previously [1d] discussed the substituent chemical shifts observed when a terminal proton in a normal alkane RH is replaced by an organotin moiety. In the tetraalkyltins I—VI, the correlation between the substituent chemical shift for the α-carbons (α-effect) and the inductive effect of the alkyl groups (σ^*) is good ($r = 0.961$).

Compounds of the type Me_3SnR can be considered as derivatives of Me_4Sn in which a methyl group is replaced by R. Compounds IX—XIV, where R is clearly electron-releasing, show a high-field shift $\Delta\delta(Me_3SnR{-}Me_4Sn)$ for the methyl carbons of 0.0—2.5 ppm, though the correlation with $\sigma^*(\text{R})$ is poor ($r = 0.718$). $\Delta\delta$ for Me_3SnCH_2Ph is anomalous on the basis of the literature Taft constant; this, combined with the anomalous values of ^1J noted above, lends support to the suggestion first made by Verdonck and van der Kelen [16] that back-donation from the benzyl group to tin occurs.

In compounds of the type $MeSnR_3$ (XXVIII—XXXII), the methyltin carbon shift can also be correlated with the inductive effect of the group R. Similar effects are noted for the methyl carbons and butyl α-carbons in compounds of the type Me_nSnBu_{4-n} (I, V, XII, XXVII, XXXI).

Examination of the chemical shifts of the t-butyl carbons in compounds of the type t-$BuSnR_3$ (XIV, XX, XXIII—XXVI) shows that the correlation between δ(C) and $\Sigma\sigma^*(R_3)$ is good for both α- and β-carbons (C_α, $r = 0.976$, C_β, $r = 0.981$); however, these carbons are shifted to low-field when the electron-releasing power of R increases, and not as expected to high field. However, when the shifts of the α-carbons of the R groups in the series R_3SnMe are compared with the same shifts in R_3Sn-t-Bu, the expected (small) high-field is observed when Me is replaced by t-Bu. In the R_3Sn-t-Bu series, the ^{119}Sn chemical shifts are as follows: R = Me, 19.5; R = Et, —0.5; R = Pr, —11.8; R = Bu, —7.9; R = i-Pr, —48.7 ppm. The trend in these values can also be explained in terms of the electron-releasing power of R. Since the relation between δ(C) and the net charge on the carbon atoms in the paraffin series is apparently also valid for alkyltin compounds, we must conclude that on going from Me_3Sn-t-Bu to i-Pr_3Sn-t-Bu a charge redistribution occurs which causes the t-butyl carbons to become slightly more positive.

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