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^{13}C and ^{119}Sn NMR spectra of some tribenzyltin(IV) compounds

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Abstract

The ^{13}C and ^{119}Sn NMR spectra of some tribenzyltin(IV) compounds and their complexes in coordinating and non-coordinating solvents have been studied. The $\delta(^{119}Sn)$ chemical shifts and coupling constants $^{1}J(^{119}Sn, ^{13}C)$ clearly depend on the coordination number of the central tin atom and the geometry of its coordination polyhedra. Approximate ranges of the characteristic values of both the NMR parameters were determined for various configurational types of tribenzyltin compound. The ^{13}C and ^{119}Sn NMR parameters found are indicative of a distinct interaction between the polarized σ(Sn–C) bond and adjacent π-electron system of the aromatic ring(s).

Introduction

In previous papers [1,2] we reported the application of ^{13}C and ^{119}Sn NMR spectra for the prediction of structure and coordination in triphenyl- and tri-n-butyltin compounds and their complexes in solutions. We revealed two different and sharply delimited regions of $\delta(^{119}Sn)$ chemical shifts characteristic on the one hand of simple pseudotetrahedral molecules R_3SnX (R = phenyl- or n-butyl- ; X = polar substituent), and on the other of trigonal-bipyramidal complexes $R_3SnX \cdot L$ (L = ligand, electron-pair donor). We also showed that it was possible to distinguish the *cis*-arrangement from the *trans*-arrangement of polar-substituents (X) and the ligands (L) about the tin atom in trigonal-bipyramidal complexes $R_3SnX \cdot L$ and to evaluate the degree of deformation of coordination polyhedra [3,4] using $^{1}J(^{119}Sn, ^{13}C)$ coupling constants. In previous papers [2,5] we described the mutual relationship of both the above-mentioned parameters for various substituents R (R = methyl, n-butyl, cyclohexyl) by linear correlation $P(R) = aP(Ph) + b$, where P is either $\delta(^{119}Sn)$ or $^{1}J(^{119}Sn, ^{13}C)$, Ph is phenyl, a and b are constants.

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The aim of this paper is to extend the knowledge on the relation between NMR parameters and shape of coordination polyhedra of organotin(IV) compounds by the investigation of another type of substituent (benzyl) in tribenzyltin(IV) compounds and their complexes and also to give a qualitative description of the presence and extent of the σ-π conjugative connection between the polarized σ(Sn–C) bond and adjacent π-electron system of the aromatic ring(s), a feature which is dependent on the composition and structure of the rest of the molecule or complex ion in the compound. Benzyltin compounds of the type of $Bz_{4-n}SnR_n$ (Bz = benzyl, R = organic substituent) have been studied several times by NMR spectroscopy, but the NMR spectra of the benzyltin compounds with polar substituents and their complexes have not yet been properly studied and the few remarks and notes available do not allow any conclusions to be made in terms of the above-mentioned goals.

Experimental

Compounds **1**–**5** and **7** (see Table 2) were prepared by published methods [6–9], and compounds **6**,**8** and **9** were prepared by procedures described [10–12] for analogous triphenyltin(IV) compounds. The identification of the compounds was carried out by elemental analysis and by ^{13}C and ^{119}Sn NMR spectroscopy. The results of elemental analysis and melting points of the compounds **6**,**8** and **9** are listed in Table 1. The ^{13}C and ^{119}Sn NMR spectra were recorded on a JNM-FX 100 spectrometer (JEOL, Japan) at 25.047 and 37.14 MHz, respectively. The compounds measured either in ca 20% (w/v), or saturated solutions (in the case of poor solubility) in deuteriochloroform ($CDCl_3$), hexadeuteriodimethyl sulphoxide (dmso-d_6), pentadeuteriopyridine (py-d_5), hexamethylphosphortriamide (hmpa) and trideuterionitromethane (CD_3NO_2). Conditions for measurement are given in refs. 1 and 2. ^{13}C chemical shifts were referred to a suitable solvent signal (δ in ppm): $CDCl_3$ ($\delta = 77.00$), dmso-d_6 ($\delta = 39.60$), py-d_5 ($\delta = 149.00$ C(2)), hmpa ($\delta = 36.00$), CD_3NO_2 ($\delta = 62.80$). ^{119}Sn chemical shifts are relative to external neat tetramethylstannane. Positive values denote down-field shifts. Temperatures given in Tables 2

Table 1

Analytical data and melting points of tribenzyltin(IV) compounds

Compound	Anal. (Found (calc) (%))				m.p. (°C)
	C	H	Sn	other	
$Et_4N^+Bz_3SnCl_2^-$	58.98 (58.71)	7.37 (6.97)	19.84 (20.01)	N 2.27 (2.36) Cl 12.13 (11.95)	149–151
$Bz_3Sn \cdot edtc$	58.04 (57.79)	5.96 (5.78)	22.12 (21.96)	N 2.33 (2.59) S 11.59 (11.87)	58–60
$Bz_3SnSnBz_3$	64.81 (64.33)	5.67 (5.40)	29.97 (30.27)		147–148

and 3 correspond to the temperature, measured with a thermocouple with an accuracy of ±1K, of air flowing through the probe.

Results and discussion

Chemical shifts $\delta(^{119}Sn)$

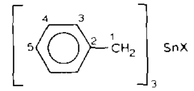
The chemical shifts $\delta(^{119}Sn)$ of the compounds studied are listed in Table 2. It

Table 2

^{119}Sn and ^{13}C chemical shifts of tribenzyltin(IV) compounds

Compound	Solvent	Temperature (K)	$\delta(^{119}Sn)$	$\delta(^{13}C)$ [a]				
				C(1)	C(2)	C(3)	C(4)	C(5)
Bz_3SnCl (**1**)	$CDCl_3$	300	51.3	25.05	137.87	127.69	128.71	124.81
	$CDCl_3$	330	50.9	25.24	137.99	127.78	128.71	124.81
	py-d_5	300	−94.1	30.79	140.93	129.04	129.04	125.04
	py-d_5	330	−73.2	30.25	140.60	128.94	128.94	125.00
	py-d_5	360	−43.8	29.57	140.25	128.99	128.99	125.09
	dmso-d_6	300	−106.3	30.73	140.39	128.11	128.11	124.01
	dmso-d_6	330	−99.4	30.54	140.14	128.01	127.81	123.77
	dmso-d_6	360	−91.2	30.34	139.95	127.86	127.62	123.62
	hmpa	300	−129.3	31.08	140.30	127.53	127.33	123.34
	hmpa	330	−124.5 [b]	30.98	140.30	127.67	127.33	123.24
Bz_3SnI (**2**)	$CDCl_3$	300	−19.1	24.66	138.50	127.69	128.71	124.71
	$CDCl_3$	330	−20.1	24.85	138.60	127.73	128.71	124.81
	hmpa	300	−124.4	32.88	140.44	127.00	127.58	123.04
$(Bz_3Sn)_2O$ (**3**)	$CDCl_3$	300	11.4	24.17	139.54	128.54	127.66	124.04
$Bz_3SnOCOMe$ (**4**)	$CDCl_3$ [c]	300	−17.2	24.12	138.51	127.73	128.61	124.42
	$CDCl_3$ [d]	330	−16.5	24.41	138.55	127.83	128.61	124.47
	hmpa [e]	300	−162.5	28.20	140.83	127.19	127.82	123.04
	hmpa [f]	330	−154.2	28.54	140.78	127.09	128.55	122.95
$Bz_3SnOCOPh$ (**5**)	$CDCl_3$ [g]	300	−12.8	24.07	138.65	127.83	128.61	124.42
	$CDCl_3$ [h]	330	−12.6	24.32	138.70	127.93	128.61	124.47
	hmpa	330	−161.2	28.06	140.88	127.09	127.92	122.85
$Et_4N^+ Bz_3SnCl_2^-$ (**6**)	CD_3NO_2 [i]	300	−141.6	34.97	142.78	128.74	129.42	124.65
	CD_3NO_2 [j]	330	−141.0	35.12	142.92	128.79	129.57	124.70
$Bz_3Sn\cdot$oxin (**7**)	$CDCl_3$ [k]	300	−94.5	28.12	140.89	127.93	128.22	123.50
	$CDCl_3$	330	−92.7	28.31	140.94	128.03	128.22	123.54
$Bz_3Sn\cdot$edtc (**8**)	$CDCl_3$ [m]	300	−92.6	26.45	140.53	127.60	128.13	123.63
	$CDCl_3$ [n]	330	−91.2	26.75	140.59	127.72	128.13	123.69
$(Bz_3Sn)_2$ (**9**)	$CDCl_3$	330	−45.9	20.81	142.60	127.30	128.61	123.79
	py-d_5	300	−43.1	20.34	142.42	126.97	128.24	123.32
	hmpa	330	−44.8 [p]	20.21	142.44	126.89	127.87	122.89

[a]



[b] $\delta(^{119}Sn) = -121.0$ at 360 K. [c] 177.59(COO), 20.86(CH_3). [d] 177.49(COO), 20.71(CH_3). [e] 173.78(COO), 22.16(CH_3). [f] 173.63(COO), 21.87(CH_3). [g] 172.33(COO), 130.95(i), 130.22(o), 128.12(m), 132.46(p)(C_6H_5). [h] 172.33(COO), 131.19(i), 130.27(o), 128.08(m), 132.36(p)(C_6H_5). [i] 53.30(CH_2), 7.73(CH_3). [j] 53.64(CH_2), 7.87(CH_3). [k] oxin = 8-hydroxyquinolinate, $\delta(^{13}C) = 156.10$, 144.45, 138.36, 137.43, 128.95, 120.77, 114.09, 113.41 ppm, (9th signal overlapped by signals of benzyl group). [m] edtc = *N*,*N*-diethyldithiocarbamate; 195.58(CSS), 49.80(CH_2), 11.83(CH_3). [n] 196.00(CSS), 49.85(CH), 11.89(CH_3). [p] $\delta(^{119}Sn) = -42.9$ at 300 K.

can be seen that the values of $\delta(^{119}Sn)$ depend significantly on the composition of the compounds, on solvent type, and in some cases, also on the temperature.

Compounds 1–5 in non-coordinating solvent (deuteriochloroform) give $\delta(^{119}Sn)$ values covering most of the range from +51.3 to −20.1, i.e. more downfield than that for tetrabenzyltin (−36 ppm) [13]. The $\delta(^{119}Sn)$ chemical shifts of $(Bz_3Sn)_2S$ and $(Bz_3Sn)_2Se$, 26.9 and −2.0 ppm, respectively, [14] are found in the same region; and $\delta(^{119}Sn)$ of Bz_3SnEt (−23 ppm) has also been found to be close to this [15]. A common feature of all these compounds is a pseudotetrahedral coordination of the central four-coordinate tin atom [13,16]. According to the literature the characteristic $\delta(^{119}Sn)$ values for four-coordinate tribenzyltin compounds can be considered to range roughly from +55 to −25 ppm.

Chemical shifts $\delta(^{119}Sn)$ of the complex anion of compound **6**, chelate complex **7** and **8** [17] and compounds **1**,**2**,**4** and **5** in solutions of coordinating solvents are shifted markedly up-field (−43.8 to −162.5 ppm). This is clearly due to coordination because all these systems contain tribenzyltin compounds with a five-coordinate tin atom. Not all of the $\delta(^{119}Sn)$ values shown in Table 2 can be considered to be "natural", only those that are do not change too much with temperature, viz. compounds **5**–**8**. A striking dependence on temperature of $\delta(^{119}Sn)$ in systems with compounds **1**,**2** and **4** in coordinating solvents provides evidence for the equilibrium

$$Bz_3SnX + S \rightleftharpoons Bz_3SnX \cdot S \qquad (1)$$

(X = Cl, I, CH_3COO; S = py-d_5, dmso-d_6, hmpa) where the value of $\delta(^{119}Sn)$ is given as a weighted average of chemical shifts $\delta(^{119}Sn)$ of both of the tribenzyltin compounds involved in the equilibrium (1). Recently we showed [18] that for systems with Bz_3SnCl or other triorganotin chlorides, in various coordinating solvents, the equilibrium (1) shifts to the right side with decreasing temperature, in favour of the reaction products, and by extrapolation [18] "natural" values of their chemical shifts $\delta(^{119}Sn)$ can be determined. In this way, we obtained the $\delta(^{119}Sn)$ values for the complex $Bz_3SnCl \cdot S$ (S = hmpa, dmso and py) as −134.5, −112.0 and −121.5 ppm, respectively. These values do not differ too much from those given in Table 2 for $\delta(^{119}Sn)$ at 300 K, and so the values at 300 K for other systems will be considered to be close to the "natural" values of $\delta(^{119}Sn)$. The above results lead to the conclusion that five-coordinate tribenzyltin compounds have chemical shifts $\delta(^{119}Sn)$ roughly in the range from −90 to −165 ppm.

The values of $\delta(^{119}Sn)$ of tribenzyltin compounds cover nearly the same broad range as those of other triorganotin compounds in regard to both the whole range and the individual ranges for the different coordination types. Furthermore, it follows that from fairly good linear correlations of $\delta(^{119}Sn)$ values for tribenzyltin compounds with analogous triphenyl- and tri-n-butyltin compounds:

$$\delta(^{119}Sn)(Bz_3Sn) = (0.86 \pm 0.03)\,\delta(^{119}Sn)(Ph_3Sn) + (78.13 \pm 4.51) \qquad (2)$$
$$N = 14,\ r = 0.994$$

$$\delta(^{119}Sn)(Bz_3Sn) = (0.95 \pm 0.09)\delta(^{119}Sn)(n\text{-}Bu_3Sn) - (96.74 \pm 21.50) \qquad (3)$$
$$N = 13,\ r = 0.956$$

(The values of $\delta(^{119}Sn)$ used for correlations (2) and (3) were taken from refs. 1,2,14,19 and from this work.)

The dependence of the $\delta(^{119}Sn)$ for tribenzyltin compounds on the same parameters as those for triphenyltin compounds is shown in Fig. 1. We can see that the

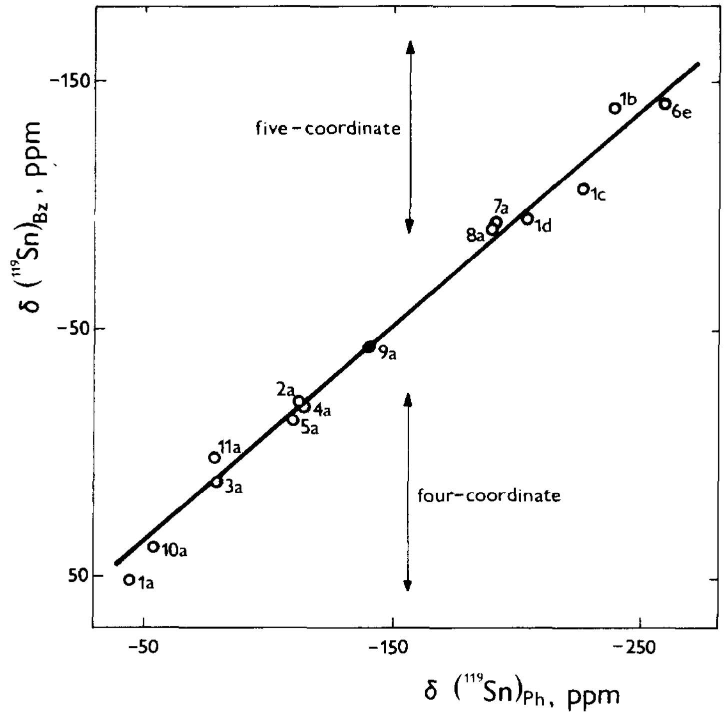


Fig. 1. The mutual dependence of chemical shifts δ (^{119}Sn) of tribenzyl- and triphenyltin(IV) compounds. The numbering of compounds is as indicated in Table 2 ($CDCl_3$ (a), hmpa (b), dmso-d_6 (c), py-d_5 (d), CD_3NO_2 (e)). The compounds $(R_3Sn)_2S$ and $(R_3Sn)_2Se$ (from ref. 14) are denoted by numbers **10** and **11**, respectively.

tribenzyltin compounds with a different coordination lie in different ranges on the δ(^{119}Sn) scale, separated from another by a wide (ca 70 ppm) gap, in which no "natural" values of δ(^{119}Sn) occur. It is noteworthy that as in the case of analogous triphenyl- and tri-n-butyltin compounds the chelate complexes **7** and **8** also reveal chemical shifts δ(^{119}Sn) close to the lower boundary of the range usually assigned to five-coordinate tribenzyltin compounds, which is characteristic of their *cis*-trigonal bipyramidal geometry [1,2], whereas the carboxylates **4** and **5** reveal values of δ(^{119}Sn) more in the upper part of the characteristic range of four-coordinate tin compounds (weak asymmetric chelates [20]).

Recently [1] we assigned the range of δ(^{119}Sn) values from −40 to −120 ppm to four-coordinate triphenyltin compounds, which includes not only pseudotetrahedral Ph_3SnX molecules with polar substituent X, but also compounds with the Ph_3Sn group bonded to a transition-metal atom, such as in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(SnPh_3)]$ (−58.2 ppm), *trans*-$[PtH(Me)(SnPh_3)_2bipy]$ (−74.2 ppm) and *cis*-$[Pt(Ph_3Sn)(Ph)(PPh_3)_2]$ (−106 ppm) [14], or to a non-transition metal in organometallic compounds ($Ph_3SnPbPh_3$ (−119.5 ppm)) [14]. The only exceptions here are compounds with an Sn–Sn bond as in $R_3SnSnR'_3$ (R = Ph, R′ = Me, Et, Ph, cyclohexyl; δ(^{119}Sn) values range from −134 to −153 ppm) [21] usually revealing a slight upfield shift of the δ(^{119}Sn) value for Ph_3Sn behind the defined range. Similar deviations from "expected" values are also observed for other R_3Sn groups in hexaorganodistannanes [21]. Thus it seems to be a more general case which as yet has not been explained. In view of this the Bz_3Sn group exhibits similar behaviour which is evidenced by the value of $\delta(^{119}Sn)$ for compound **9** and its position in the correlation equation (2), and can be seen in Fig. 1. This of course provides evidence for the pseudotetrahedral coordination of the tin atom in compound **9** not only in solutions of non-coordinating deuteriochloroform, but also in other coordinating solvents (see Table 2). This fact manifests the reluctance of these compounds to form complexes with a tin atom of higher coordination number. For other compounds with the Bz_3Sn group bonded to a metal, in accordance with the analysis given above, we presume that the values of $\delta(^{119}Sn)$ for four-coordinate tin compounds of the Bz_3SnX type lie within the range from + 55 to − 25 ppm.

Coupling constants $^nJ(^{119}Sn, ^{13}C)$ and $^nJ(^{119}Sn,H)$

The coupling constants $^nJ(^{119}Sn, ^{13}C)$ and $^nJ(^{119}Sn,H)$ are listed in Table 3.

Table 3

$^nJ(^{119}Sn, ^{13}C)$ and $^nJ(^{119}Sn,H)$ coupling constants of tribenzyltin(IV) compounds

Compound ^{a}	Solvent	Temperature (K)	$^2J(^{119}Sn,H)$ (Hz)	$^nJ(^{119}Sn, ^{13}C)$ (Hz)				
				$n = 1$	2	3	4	5
1	$CDCl_3$ ^{b}	300	66.1	293.0	42.7	31.8	18.0	20.8
	$CDCl_3$	330	66.1	294.2	44.0	31.7	18.0	21.0
	py-d_5	300	76.1	415.0	52.5	34.2	18.0	22.0
	py-d_5	330	74.7	396.7	51.9	34.2	18.3	21.3
	py-d_5	360	72.7	374.8	51.3	34.2	18.3	21.3
	dmso-d_6 ^{c}	300	80.9	429.6	53.7	34.2	18.3	22.0
	dmso-d_6	330	80.6	427.2	52.5	34.2	18.0	22.0
	dmso-d_6	360	80.1	420.0	52.0	34.2	18.0	22.0
	hmpa	300	^{d}	460.2	53.7	36.6	19.0	22.0
	hmpa	330	^{d}	454.1	52.9	36.6	18.0	22.0
2	$CDCl_3$	300	63.0	273.4	43.0	31.7	18.3	20.8
	$CDCl_3$	330	63.0	273.4	43.1	31.8	17.9	21.4
	hmpa	300	^{d}	432.1	54.9	36.6	18.0	22.0
3	$CDCl_3$	300	^{d}	318.0	39.6	29.4	14.6	18.0
4	$CDCl_3$	300	71.0	315.0	40.3	31.8	17.0	20.8
	$CDCl_3$	330	71.0	313.7	40.3	31.8	17.0	20.8
4	hmpa	300	^{a}		51.7	36.0	17.0	20.8
	hmpa	330	^{d}	470.0	51.9	35.2	17.0	20.8
5	$CDCl_3$	300	71.5	316.8	40.3	31.8	17.0	20.8
	$CDCl_3$	330	71.5	317.4	40.3	31.8	17.1	20.8
6	CD_3NO_2	300	84.0	455.3	54.9	34.8	18.3	22.0
	CD_3NO_2	330	84.0	455.3	54.9	35.4	18.6	22.0
7	$CDCl_3$	300	70.8	344.2				20.8
	$CDCl_3$	330	69.8	345.5				20.8
8	$CDCl_3$	300	66.4	303.3	41.5	30.8	17.6	22.0
	$CDCl_3$	330	66.4	303.3	41.5	30.8	17.6	22.0
9	$CDCl_3$ ^{e}	330	51.3	181.9	35.4	24.4	13.4	15.9
	py-d_5 ^{f}	300	52.2	180.7	35.4	23.8	13.4	16.4
	hmpa ^{g}	330	^{d}	180.7	35.4	24.4	14.0	16.6

^{a} See Table 2. ^{b} $^1J(^{13}C,H)$ 134.7 Hz. ^{c} $^1J(^{13}C,H)$ 133.7 Hz. ^{d} Overlap. ^{e} $^3J(^{119}Sn,H)$ 11.2 Hz, $^2J(^{119}SnSn^{13}CH_2)$ 36.6 Hz, $^1J(^{119}Sn, ^{117}Sn)$ 1733.4 Hz, $^1J(^{119}Sn, ^{119}Sn)$ 1814.0 Hz. ^{f} $^3J(^{119}Sn,H)$ 12.1 Hz, $^2J(^{119}SnSn^{13}CH_2)$ 36.6 Hz, $^1J(^{119}Sn, ^{117}Sn)$ 1738.3 Hz, $^1J(^{119}Sn, ^{119}Sn)$ 1819.1 Hz. ^{g} $^2J(^{119}SnSn^{13}CH_2)$ 36.0 Hz, $^1J(^{119}Sn, ^{117}Sn)$ 1647.9 Hz, $^1J(^{119}Sn, ^{119}Sn)$ 1724.5 Hz.

The coupling constants $^1J(^{119}Sn, ^{13}C)$ of the studied compounds range from about 180 to 460 Hz and depend significantly on the geometry of the vicinity of central tin atom. The highest value was found for the $Bz_3SnCl_2^-$ anion in compound **6** (~ 455 Hz). This value closely approaches the coupling constants $^1J(^{119}Sn, ^{13}C)$ of compounds **1**,**2**,**4** and **5** in coordinating solvents (374.8–460.2 Hz). These values, however, as a result of their temperature dependence, are affected by equilibrium (1) as are the values of $\delta(^{119}Sn)$ for these compounds (see above). The "natural" values of $^1J(^{119}Sn, ^{13}C)$, regarded by us as such when measured at ~ 300 K, lie within the relatively narrow band 415–460 Hz. The simple compounds **1**–**5** in non-coordinating solvent ($CDCl_3$) and the chelate complexes **7** and **8** reveal substantially lower coupling constants $^1J(^{119}Sn, ^{13}C)$ from 273.1 to 345.2 Hz. The lower limit of this range approaches the value of 257.9 Hz for the compound, Bz_4Sn [22]. Similarly, for the triphenyl- and tri-n-butyltin compounds [1,2] we ascribe the $^1J(^{119}Sn, ^{13}C)$ values within the range of 415 to 460 Hz to the *trans*-trigonal bipyramidal coordination of the central tin atom in five-coordinate complexes where the bonds of C(1) atoms of benzyl groups with central tin atoms (sp^2 hybrid orbitals) form an equatorial plane, while the polar substituents X and donor atoms of ligands L (chlorine atom in the compound **6** or the donor atom of solvent S) are axial (three-centre orbital) [23]. The lower values of $^1J(^{119}Sn, ^{13}C)$ (~ 270 to 345 Hz) are attributed to the pseudotetrahedral molecules of the simple compounds Bz_3SnX (sp^3 hybrid orbitals of tin atom) and *cis*-trigonal bipyramidal chelates, (one of the sp^3 hybrid orbitals of central tin atom participates in bonding with two donor centres of bidentate ligand using the bent three-centre molecular orbital [23]) as a result of lower *s*-electron contribution to the Sn–C bond. Assuming that the linear relations between the values of $|^1J(^{119}Sn, ^{13}C)|$ and C–Sn–C bond angles (θ) [3] are valid, the value of 257.9 Hz of the coupling constant of Bz_4Sn would correspond to $\theta = 109.5°$ [24] and that of ~ 460 Hz to $\theta = 120°$. However, it is evident that replacement of a benzyl group in Bz_4Sn by a more polar group X leads to an increase in repulsion between the organic substituents and the opening of the angle θ which results in an increase in the value of the coupling constant $^1J(^{119}Sn, ^{13}C)$. Solutions of compounds **1**–**5** in deuteriochloroform were estimated to have a value of $\theta = 111–113°$, which is in good agreement with the value of ~ 110° determined from the diffraction data for compound 3 in the crystalline state [9]. Non-equivalent action by ligands L and polar substituents X results in slightly smaller values of θ and hence in the $^1J(^{119}Sn, ^{13}C)$ coupling constants of trans-trigonal bipyramidal complexes than the ideal theoretical value of ~ 460 Hz corresponding to the angle θ 120°. The deviation of coordination polyhedra of both types of compound from ideal geometry are, however, relatively small. But the shape of the polyhedra of chelate complexes **7** and **8** ($\theta \sim 114$ and 112°, respectively) deviate significantly from the ideal *cis*-trigonal bipyramidal geometry. Similar conclusions relating to the shape of the coordination polyhedra can be made from the values of $^2J(^{119}Sn,H)$, because these values correlate well (linearly) with the values of $^1J(^{119}Sn, ^{13}C)$ by the expression (4):

$$^2J(^{119}Sn,H) = (0.11 \pm 0.01)\,^1J(^{119}Sn, ^{13}C) + (31.81 \pm 2.1) \qquad (4)$$

$$N = 12, \; r = 0.983$$

The coupling constants $^1J(^{119}Sn, ^{13}C)$ of benzyltin compounds have generally lower values than those of most of the other organotin(IV) compounds. This fact is usually ascribed to a decrease in the *s*-electron character of the Sn–C(1) bond (in comparison with alkyltin compounds) at the expense of increasing *s*-electron character and bond order of the C(1)–C(2) bond owing to the conjugation of polarized Sn–C(1) bond with the π-electron system of the adjacent aromatic ring [25]. The geometrical similarity of polyhedra of the studied tribenzyltin and analogous n-butyltin compounds allows a close comparison and evaluation to be made of the degree of σ-π conjugative interaction (hyperconjugation) in the tribenzyltin compounds as a function of the nature of polar substituents X or the ligand L. The values of $^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ of the studied tribenzyltin compounds (including the compound Bz_4Sn) exhibit an excellent correlation with those of analogous n-butyltin compounds (the values of $^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ of n-butyltin(IV) compounds for the correlation are taken from refs. 2,21 and 22). From correlation (5) it is obvious, that all benzyltin compounds exhibit lower $^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ values than the corresponding n-butyltin compounds but at the same time the slope of the straight line (gradient is greater than 1) shows that the values of $^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ for the benzyltin compounds increases more rapidly than those of n-butyltin compounds. Thus with increasing values of $^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ differences between coupling constants $^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ of n-butyl- and benzyltin(IV) analogues decrease. Thus with increasing electronegativity of the substituent X and with increasing participation and strength of the donor–acceptor interaction Sn←L the contribution of σ-π hyperconjugation in the compounds decreases. The strikingly low value of $^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ of the compound **9** is not exceptional. Generally lower $^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ values for hexaorganoditin(IV) compounds R'_3SnSnR_3 [21] (in comparison with the compounds R_3SnX with an electronegative substituent X) are due to a lower *s*-electron contribution to the Sn–C(1) bond caused by the presence of an adjacent electron-releasing R'_3Sn group.

$$^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})(\mathrm{Bz_3Sn}) = (1.12 \pm 0.01)\,^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})(\mathrm{n\text{-}Bu_3Sn}) - (91.91 \pm 4.61) \qquad N = 12,\ r = 0.999 \tag{5}$$

The coupling constants $^2J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ and $^3J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ are not significantly affected by the nature of substituent X, or by changes in the coordination, the shapes of hybrid orbitals of the tin atom or the contribution of *s*-electron density, these lead, like those for the $^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ coupling constant, to an increase of ~ 10 Hz in $^2J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ and of ~ 2–4 Hz in $^3J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$.

The coupling constants $^4J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ and $^5J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ with the compounds studied except **3** and **9**, have almost constant values, 18.0 ± 1.0 and 21.4 ± 0.6 Hz, respectively. A rather high $^5J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ value especially if it is higher than that of $^4J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$, is characteristic of the σ-π hyperconjugative connection of the polarized Sn–C(1) bond with adjacent π-electron system of the aromatic ring [26,27]. The efficiency of this connection depends on the geometrical arrangement of the fragment $Sn–CH_2–C_6H_5$. In an ideal case the plane containing the Sn–C(1) bond is perpendicular to the plane of the aromatic system (dihedral angle of the plane Sn–C(1)–C(2)–C(3) is 90°). Dihedral angles of 60° and 0° (in compounds where the group $(CH_3)_3SnCH_2$ is bonded to various aromatic systems) were ascribed $^5J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ values of 15 and 0–5 Hz, respectively [26,27]. The $^5J(^{119}\mathrm{Sn}, ^{13}\mathrm{C})$ values of the compounds studied being ~ 21.5 Hz, and in view of the previous statement, could correspond to angles close to an ideal arrangement (angles θ ~ 90°). However, it is not known by how much the coupling constants $^5J(^{119}\mathrm{Sn},

^{13}C) are affected by the composition of the rest of the molecule or by the complex ions linked to the Sn–C(1)–C_6H_5 fragment, i.e. the effect of the nature of substituents X or ligands L. For di- and monobenzylmercury compounds, Bz_2Hg and BzHgX, the values of ^5J(^{119}Sn, ^{13}C) differ significantly [26]. Nevertheless the values of ^5J(^{119}Sn, ^{13}C), given their slight dependence on composition and nature of substituents X and ligands L and the fact that ^5J(^{119}Sn, ^{13}C) values are always higher than ^4J(^{119}Sn, ^{13}C) values, led us to the conclusion that in the compounds studied there are also highly favourable geometrical conditions for σ-π hyperconjugation of the Sn–C(1) bond with the aromatic system. From the diffraction data obtained [8,9,24] for three benzyltin compounds in crystalline state, we have calculated the average dihedral angles to be 81.5° (Bz_4Sn), 88° ($(Bz_3Sn)_2O$) and 77° ($Bz_3SnOCOMe$).

Chemical shifts $\delta(^{13}C)$

The effect of σ-π hyperconjugation of Sn–C(1) bond with aromatic ring of benzyl group in the compounds studied can also be observed in the values of their $\delta(^{13}C)$ chemical shifts. It can be seen from Table 4, where ^{13}C substituent chemical shifts (SCS) of the compounds studied are presented as the difference between the $\delta(^{13}C)$ values from Table 2 and the chemical shifts $\delta(^{13}C)$ of toluene at 300 K.

It is evident that replacement of a hydrogen atom in the methyl group of toluene by an R^x group (the rest of the molecule or complex ion in compounds **1**–**9** and other model compounds with the exception of one benzyl group, i.e. Me_3Sn, Bz_3Sn, Bz_2SnX, $Bz_3SnSnBz_2$ or $Bz_2Sn(X) \cdot L$, significantly affects resonance positions.

Table 4

^{13}C SCS values of tribenzyltin(IV) compounds at 300 K (referred to toluene [a])

Compound [b]	Solvent	^{13}C SCS, ppm				
		C(1)	C(2)	C(3)	C(4)	C(5)
$BzSnMe_3$ [c]	$CDCl_3$	−1.44	5.29	−2.41	−0.07	−2.44
Bz_4Sn [d]	$CDCl_3$	−2.68	3.61	−1.70	0.30	−1.81
1	$CDCl_3$	3.66	0.10	−1.31	0.54	−0.49
	py-d_5	9.40	3.16	0.04	0.87	−0.26
	dmso-d_6	9.34	2.62	−0.89	−0.06	−1.29
	hmpa	9.69	2.53	−1.47	−0.84	−1.96
2	$CDCl_3$	3.27	0.73	−1.31	0.54	−0.59
	hmpa	11.49	2.67	−2.00	−0.59	−2.26
3	$CDCl_3$	2.78	1.77	−0.46	−0.51	−1.26
4	$CDCl_3$	2.73	0.74	−1.27	0.44	−0.88
	hmpa	6.81	3.06	−1.81	−0.35	−2.26
5	$CDCl_3$	2.68	0.88	−1.17	0.44	−0.88
	hmpa [e]	6.67	3.11	−1.91	−0.25	−2.45
6	CD_3NO_2	13.58	5.01	−0.26	1.25	−0.65
7	$CDCl_3$	6.73	3.12	−1.07	0.05	−1.80
8	$CDCl_3$	5.06	2.76	−1.40	−0.04	−1.67
9	$CDCl_3$ [e]	−0.58	4.83	−1.70	0.44	−1.51
	py-d_5	−1.05	4.65	−2.03	0.07	−1.98
	hmpa [e]	−1.18	4.67	−2.11	−0.30	−2.41

[a] $\delta(^{13}C)$ toluene: 21.39(C(1)), 137.77(C(2)), 129.00(C(3)), 128.17(C(4)), 125.30(C(5)), 21.39(CH_3). [b] See Table 2. [c] Ref. 26. [d] Ref. 29. [e] 330 K.

Negative values of ^{13}C SCS of C(3) and C(5) atoms (*o*- and *p*-position of the phenyl ring) indicate that R^xCH_2 substituents in all compounds studied act as resonance donors towards the aromatic ring. The ^{13}C SCS values for the C(5) atom in four-coordinate compounds $BzSnMe_3$, Bz_4Sn and in compounds **1**–**5** and **9** in $CDCl_3$ lie in the range from −0.49 to −2.44 ppm which is strictly dependent on the composition of the substituent R^x. These values for Bz_4Sn and for compound **9**, in which the substituents R^x are composed of purely organic (Bz) and/or organometallic (Bz_3Sn, Bz) electron-releasing groups only, approach the ^{13}C SCS value of (C(5)) in the model compound $BzSnMe_3$ [26]. The large decrease (−0.44 to −1.26 ppm) of this value is observed in compounds **1**–**5**, with substituents R^x which range from organic (Bz) to polar (Cl, I, MeCOO, PhCOO, Bz_3O). Similar changes (depending on the composition of the substituent R^x) can be seen also in ^{13}C SCS values for atoms C(3). The ^{13}C SCS values for C(4) atoms are very low for all of the four-coordinate compounds studied, nevertheless, their increase (the shift to higher field) occurs with the replacement of the organic group by a polar one in the substituent R^x. Thus the resulting donor effect of the R^x substituent in compounds **1**–**5** is decreased by the inductive action of the electron-attracting group X present. The opposite action of the inductive effect is observed in five-coordinate complexes with the *trans*-trigonal bipyramid coordination of the central tin atom (compounds **1**–**5** and to a lesser extent also compound **9** in coordinating solvents). Their ^{13}C SCS values for C(3), C(4) and C(5) atoms are all shifted upfield, the largest shift (in comparison with simple compounds **1**–**5** and **9** from which they are derived) being observed for C(4) atoms. The inclusion of the ligand L into the coordination sphere of the central tin atom (resulting in an increase in its coordination number) is associated with an increased electron density on the tin atom and thus the increased donor capability of the R^xCH_2 substituents ($R^x = Bz_2Sn(X) \cdot L$). When comparing ^{13}C SCS of C(4) and C(5) atoms the resonance donor effect in five-coordinate compounds (*trans*-) appear to be even lower than those in four-coordinate compounds. The contribution of the inductive donor effect of ligands L to the increased donor capability of *trans*-trigonal bipyramid five-coordinate substituents R^xCH_2 is markedly higher than that of the resonance effect. The ^{13}C SCS of C(3), C(4) and C(5) atoms in chelate complexes **7** and **8** indicate relatively strong and pure resonance donor capability of substituents R^x derived from these compounds. The exceptional behaviour shown by complex **6** and compound **1** (in pyridine) is probably associated with the specific properties of ligands L (feeble donor capability of Cl^- anion, σ-donor and π-acceptor properties of pyridine). ^{13}C SCS analysis of the C(1) and C(2) atoms is very difficult, because of the inverse dependence of their values on the σ- and π-electron population on the carbon atoms [28]. The ^{13}C SCS values for both the carbon atoms are nearly identical with those for the C(1) and C(2) atoms in n-butyltin(IV) compounds (calculated as the difference between $\delta(^{13}C)$ of n-butyltin(IV) compounds [2] and of $\delta(^{13}C)$ of the n-butane) and also reveal practically the same trends in the dependence on the composition by the compounds. It follows from this that the ^{13}C SCS values for C(1) and C(2) predominantly reflect the inductive and coordination effects, as discussed in refs. 1 and 2.

If the resonance donor effects of substituents R^xCH_2 in benzyltin compounds are caused mainly by σ-π conjugation of the Sn–C(1) bond with the aromatic system, we can make a similar conclusion about the participation of this type of conjugation and its contribution, as in the analysis of $^1J(^{119}Sn, ^{13}C)$ values (see above).

Conclusions

The various shapes of coordination polyhedra of the tribenzyltin(IV) compounds can be distinguished by their ^{13}C and ^{119}Sn NMR spectral parameters, especially the $\delta(^{119}Sn)$ and $^{1}J(^{119}Sn, ^{13}C)$ values. The chemical shifts $\delta(^{119}Sn)$ of simple (pseudo)tetrahedral compounds lie in range of $+55$ to -25 ppm. For five-ccordinate complexes $\delta(^{119}Sn)$ values are substantially higher (-90 to -165 ppm). The coupling constants $^{1}J(^{119}Sn, ^{13}C)$ of compounds with tetrahedral and *cis*-trigonal bipyramid arrangements of the central tin atom display values from ca. 180 to 345 Hz. The higher values (415–460 Hz) are typical of *trans*-trigonal bipyramid complexes.

The geometrical arrangement of the $Sn{-}CH_2{-}C_6H_5$ fragment in all the compounds under study is conducive to the formation of σ-π conjugative connection of the σ(Sn–C) bond with the π-electron system of the aromatic ring(s). The extent of this conjugation decreases in the series $Bz_3SnR >$ *cis*-$Bz_3SnX \cdot L$(chelate) $\approx Bz_3SnX >$ *trans*-$Bz_3SnX \cdot L$ in accordance with decreasing *p*-electron character of the Sn–C bond and is probably due to this decrease, see ref. 30.

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