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THE ^{13}C AND ^{119}Sn NMR SPECTRA OF SOME FOUR- AND FIVE-COORDINATE TRI-n-BUTYLTIN(IV) COMPOUNDS

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Summary

The ^{13}C and ^{119}Sn NMR spectra of a set of tri-n-butyltin(IV) compounds and their complexes in coordinating and non-coordinating solvents have been studied. The chemical shifts $\delta(^{119}\mathrm{Sn})$ and $\delta(^{13}\mathrm{C})$ and the coupling constants $^1J(^{119}\mathrm{Sn}^{13}\mathrm{C})$ depend significantly on the coordination number of the tin atom and on the geometry of its coordination sphere. Approximate ranges of these characteristic NMR parameters for various types and configurations of tri-n-butyltin(IV) compounds have been defined. The data for these compounds are discussed in comparison with those for triphenyltin(IV) compounds.

Introduction

In a previous paper [1] we suggested the possibility of distinguishing between various types of coordination and configuration of triphenyltin(IV) compounds and their complexes in coordinating and non-coordinating solvents using characteristic values of their ^{13}C and ^{19}Sn NMR spectra. In this paper we report a study of ^{13}C and ^{119}Sn NMR spectra of tri-n-butyltin(IV) compounds, and show that the method of distinguishing between various structural types of triphenyltin(IV) compounds [1–3] can be applied also to other triorganotin compounds.

Experimental

All the compounds (see Tables 1 and 2) were prepared by published methods [4–10]. The ^{13}C and ^{119}Sn NMR spectra were measured on the JEOL (Japan) spectrometer JNM-FX 100 at 25.047 and 37.14 MHz, respectively, at 300 K. The ^{119}Sn chemical shifts are related to external neat $(CH_3)_4Sn$ and the ^{13}C chemical

(Continued on p. 46)

TABLE 1

^{119}Sn NMR PARAMETERS FOR TRI-n-BUTYLTIN(IV) COMPOUNDS

No.	Compound	Solvent	$\delta(^{119}\mathrm{Sn})$(ppm)		$^nJ(^{119}\mathrm{Sn}^{13}\mathrm{C})$ (Hz)[c]		
			a	b	$n=1$	$n=2$	$n=3$
1	n-Bu_3SnCl	(neat)	–	144.0	345.5	25.6	65.8
		$CDCl_3$[d]	–	152.8	339.5	23.4	64.5
		py-d_5[e]	5.6	10.6	449.2	29.3	75.6
		dmso-d_6[f]	2.9	2.7	464.4	28.6	73.8
		hmpa[g]	−37.9	−35.1	491.5	26.4	79.2
2	n-Bu_3SnBr	(neat)	–	133.2	330.8	23.2	63.5
		$CDCl_3$	142.2	141.6	326.7	23.4	64.4
		py-d_5	3.8	5.6	441.9	29.3	78.1
		dmso-d_6	3.8	5.3	454.8	28.2	74.8
		hmpa[e]	−33.3	−34.1	482.0	29.3	80.6
3	n-$Bu_3SnOC(O)Me$	$CDCl_3$	106.9	104.8	360.7	20.7	67.7
		py-d_5	−3.8	−1.8	449.2	26.9	76.2
		dmso-d_6[h]	−17.6	0.5	459.0	26.8	73.2
		hmpa	−58.0	−55.5	504.0	28.0	80.6
4	n-$Bu_3SnOC(O)Ph$	(neat)	–	99.4	365.0	22.0	62.2
		$CDCl_3$	113.4	112.7	357.7	22.0	64.0
		py-d_5	−12.3	−10.0	459.0	26.2	78.2
		dmso-d_6	−21.1	−19.2	476.0	28.1	74.0
		hmpa	−60.9	−59.2	509.0	28.9	79.2
5	$Bu_3SnOCOC_6H_3(NO_2)_2$-3,5	$CDCl_3$	–	140.0	351.6	22.0	66.0
		dmso-d_6	–	−22.4	481.0	28.1	78.0
6	$[Bu_3SnO]_2CrO_2$	$CDCl_3$[d]	–	141.8	386.7	23.5	71.6
		py-d_5	27.5	26.6	454.1	24.2	78.1
		dmso-d_6	20.4	20.2	466.3	24.4	78.1
		hmpa	−15.3	−13.4	485.8	26.8	80.4
7	$[Bu_3Sn]_2O$	(neat)	–	82.4	370.4	20.3	58.1
		$CDCl_3$[d]	–	92.7	365.8	18.7	62.9
		py-d_5	85.1	84.6	373.5	20.7	70.0
		hmpa	60.6	62.2	387.5	22.0	71.2
8	$Bu_3SnCl/(Bu_3Sn)_2O$ (1/1)	(neat)	–	91.2	372.7	22.0	61.0
		$CDCl_3$	–	97.0	358.9	19.4	62.8
9	Bu_3Sn edtc[i]	(neat)	–	12.0	352.8	22.0	66.0
		$CDCl_3$	24.4	23.4	350.2	20.6	67.4
		py-d_5	15.1	14.4	356.1	22.0	67.4
		hmpa	−23.7	−19.0	413.2	24.9	76.2
10	Bu_3Sn oxin	(neat)	–	30.1	393.0	17.0	63.4
		$CDCl_3$	38.2	37.6	390.6	18.3	68.4
		py-d_5	26.6	26.8	395.5	19.5	67.2
		hmpa	−16.7	−13.3	444.3	23.2	72.0

[a] Concentration ca. 100 mg of sample/2 ml of the solvent. [b] Concentration ca. 500 mg/2 ml. [c] $^4J(^{119}\mathrm{Sn}^{13}\mathrm{C}) < 5$ Hz. [d] Ref. 8. [e] Pentadeuteriopyridine. [f] Hexadeuteriodimethyl sulphoxide. [g] Hexamethylphosphortriamide. [h] 330 K. [i] *N,N'*-Diethyldithiocarbamate.

TABLE 2

^{13}C NMR CHEMICAL SHIFTS

Compound No. ^{a}	Solvent	δ(^{13}C) (ppm)				
		C(1)	C(2)	C(3)	C(4)	others
1	(neat)	17.59	27.88	26.81	13.50	
	CDCl$_3$ ^{b}	17.30	27.60	26.50	13.30	
	py-d_5	21.09	29.03	27.52	14.22	
	dmso-d_6	21.09	27.87	26.41	13.75	
	hmpa	21.32	27.75	26.47	13.22	
2	(neat)	17.25	27.72	26.66	13.22	
	CDCl$_3$	17.20	28.16	26.67	13.48	
	py-d_5	21.77	29.23	27.38	14.12	
	dmso-d_6	21.85	28.11	26.35	13.72	
	hmpa	22.20	27.90	26.32	13.13	
3	CDCl$_3$	16.27	27.73	26.95	13.50	176.76(COO); 21.29(CH$_3$)
	py-d_5	18.41	28.79	27.62	14.07	174.32(COO); 23.09(CH$_3$)
	dmso-d_6	18.01	27.46	26.30	13.28	174.36(COO); 22.35(CH$_3$)
	hmpa	18.60	27.67	26.64	13.19	173.19(COO); 22.21(CH$_3$)
4	(neat)	16.42	27.83	26.45	13.50	171.16(COO); 132.12(C$_i$); 130.08(C$_o$); 127.74(C$_m$); 131.69(C$_p$)
	CDCl$_3$	16.52	27.78	26.90	13.55	171.94(COO); 131.93(C$_i$); 130.07(C$_o$); 127.93(C$_m$); 131.93(C$_p$)
	py-d_5	18.80	28.84	27.57	14.07	171.59(COO); 135.57(C$_i$); 130.55(C$_o$); 128.55(C$_m$); 131.82(C$_p$)
	dmso-d_6	18.59	27.76	26.49	13.62	169.78(COO); 134.73(C$_i$); 129.23(C$_o$); 127.86(C$_m$); 130.98(C$_p$)
	hmpa	18.89	27.71	26.59	13.19	168.81(COO); 135.52(C$_i$); 128.94(C$_o$); 127.09(C$_m$); 129.96(C$_p$)
5	CDCl$_3$	16.57	27.39	26.61	13.11	136.21(C$_i$); 129.25(C$_o$); 147.96(C$_m$); 120.72(C$_p$); 165.99(COO)
	dmso-d_6	19.03	28.05	26.89	13.72	139.46(C$_i$); 128.93(C$_o$); 148.23(C$_m$); 120.36(C$_p$); 164.95(COO)
6	CDCl$_3$	19.10	27.90	27.20	13.70	
	py-d_5	19.82	29.08	27.91	14.36	
	dmso-d_6	19.33	27.85	26.78	13.82	
	hmpa	22.31	30.79	29.81	13.36	
7	(neat)	16.13	28.12	27.10	13.59	
	CDCl$_3$ ^{b}	16.00	27.90	27.00	13.00	
	py-d_5	16.60	28.59	27.62	14.02	
	hmpa	16.14	27.72	26.67	13.13	
8	(neat)	17.00	28.07	27.00	13.50	
	CDCl$_3$	18.57	27.78	28.85	13.30	
9	(neat)	17.48	28.71	26.90	13.50	196.73(CS); 49.25(CH$_2$); 11.86(CH$_3$)
	CDCl$_3$	17.50	28.74	26.98	13.56	197.11(CS); 49.39(CH$_2$); 11.75(CH$_3$)
	py-d_5	18.21	29.38	27.51	14.00	197.46(CS); 49.86(CH$_2$); 12.30(CH)$_3$
	hmpa	18.62	28.34	26.64	13.13	198.58(CS); 48.17(CH$_2$); 11.55(CH$_3$)
10	(neat)	19.79	28.12	27.00	13.50	157.81; 143.33; 139.73; 136.46; 129.05 128.76; 120.57; 113.85; 113.41
	CDCl$_3$	19.93	28.12	27.14	13.64	157.61; 143.72; 139.77; 136.70; 129.15; 128.81; 120.86; 113.80(2C)

TABLE 2 (continued)

Compound No. [a]	Solvent	$\delta(^{13}C)$ (ppm)				
		C(1)	C(2)	C(3)	C(4)	others
	py-d_5	20.55	28.69	27.62	14.04	158.67; 144.95; 140.45; 137.42, 129.92; 129.48; 121.73; 114.37(2C)
	hmpa	20.21	27.76	26.64	13.19	158.96; 144.20; 140.25; 136.35; 129.18; 127.82; 120.90; 113.30; 112.71

[a] See Table 1. [b] Ref. 8.

shifts determined relative to a suitable signal of solvent and converted to the δ scale: $CDCl_3$ (77.00 ppm), pentadeuteriopyridine (δ(C(2)) 149.90 ppm), hexadeuteriodimethyl sulphoxide (39.60 ppm) and hexamethylphosphortriamide (36.00 ppm). The value of 13.50 was attributed to the methyl groups in compounds **1**–**10** when measured as neat liquids. Positive values of the chemical shifts denote downfield shifts. ^{13}C chemical shifts were assigned on the basis of the signal intensity in proton-decoupled spectra, multiplicity in proton-coupled spectra and using the known relation $^3J(^{119}Sn^{13}C) > {}^2J(^{119}Sn^{13}C)$ [8].

Results

The ^{13}C and ^{119}Sn NMR parameters for the tri-n-butyltin(IV) compounds and their complexes in neat liquids and in solutions of non-coordinating ($CDCl_3$) and coordinating solvents (pentadeuteriopyridine, hexadeuteriodimethyl sulphoxide, hexamethylphosphortriamide) are listed in Table 1 and 2. The $\delta(^{119}Sn)$ chemical shifts were measured at two different concentrations (~ 100 and 500 mg of sample in 2 ml of solvent), and the other NMR parameters refer to solutions of ~ 500 mg of sample in 2 ml of solvent.

^{119}Sn chemical shifts

The chemical shifts $\delta(^{119}Sn)$ for the studied compounds lie in the broad range -60.9 to $+152.8$ ppm, and for the individual compounds they depend on the solvent type and on the concentration. The change in the chemical shifts with the solvent type was especially evident for compounds **1**–**6**. Their chemical shifts $\delta(^{119}Sn)$ for the neat liquids and the $CDCl_3$ solutions have values varying from 99.4 to 152.8 ppm, which are typical of a quasitetrahedral arrangement of a simple trialkyltin compound with a four-coordinate tin atom [11]. The chemical shifts for the compounds **1**–**6** in $CDCl_3$ are slightly downfield (8–13 ppm) relative to those in the neat liquid, and this shift increases with decreasing concentration of the solution (by 0.5–2.1 ppm for solutions diluted 5-fold). The observed dilution effect is probably caused by a weak association of molecules of the compounds in neat liquid and their progressive dissociation upon the dilution by non-coordinating solvents, according to the equilibrium reaction

$$(Bu_3SnX)_m \rightleftharpoons m Bu_3SnX \qquad (1)$$

(Bu = n-butyl)

The downfield shift of $\delta(^{119}Sn)$ on going from the neat liquids to solutions and upon further dilution are relatively small and so equilibrium 1 must lie substantially over to the right side, towards free molecules. Thus we can assume that the values of $\delta(^{119}Sn)$ for diluted solutions (100 mg/2 ml in Table 1) are close to those for free non-coordinated (non-associated) molecules of compounds **1**–**6**. A higher degree of association can be expected only in concentrated solutions at low temperatures. The final stage of association is the polymeric structure of crystals of some of these compounds, as observed, for example, by vibrational spectroscopy [12,13] and Mössbauer spectroscopy [14].

The chemical shifts $\delta(^{119}Sn)$ for compounds **1**–**6** in coordinating solvents show a considerable upfield shift relative to non-coordinated molecules, into the range of $+27.5$ to -60.9 ppm. The upfield shift of $\delta(^{119}Sn)$ by 100–190 ppm and increasing shielding in coordinating solvents in the series pentadeuteriopyridine < hexadeuteriodimethyl sulphoxide ≪ hexamethylphosphortriamide is characteristic of the formation of complexes of triorganotin compounds with one donor molecule (e.g. molecule of the coordinating solvent) [1,3,15], and thus for the change from four-coordinate to five-coordinate tin. The values of $\delta(^{119}Sn)$ in coordinating solvents also depend on the concentration of the solution; in this case the diluted solutions almost always show small upfield shifts in $\delta(^{119}Sn)$ which can be ascribed to the existence of equilibrium reaction

$$Bu_3SnX + D \rightleftharpoons Bu_3SnX \cdot D \tag{2}$$

where D is the donor molecule. Equilibrium 2 is shifted substantially to the right in favour of $Bu_3SnX \cdot D$ complexes.

Compound **7** in neat liquid and in $CDCl_3$ solution exhibits chemical shifts close to those of compound **1**–**6**. Thus the grouping Bu_3SnO has also a quasitetrahedral structure with a four-coordinate tin atom. In pentadeuteriopyridine and hexamethylphosphortriamide $\delta(^{119}Sn)$ is little changed, i.e. equilibrium 2 for this compound is substantially shifted to the left away from the complex. The inability of compound **7** to form donor–acceptor complexes with tin playing the role of acceptor was observed by Tsvetkov et al. [16], who however, noted on the other hand, the ability of compound **7** to behave like a Lewis base with the donor center on the oxygen atom. Our attempt to prepare the donor–acceptor complex $(Bu_3Sn)_2O \cdot Bu_3SnCl$ (compound **8**) with $(Bu_3Sn)_2O$ as a Lewis base (oxygen donor) and Bu_3SnCl as a Lewis acid (tin acceptor) was unsuccesful. Contrary to expectation an equimolar mixture of both the components and their solutions in $CDCl_3$ exhibited only one $\delta(^{119}Sn)$ signal, with values of 91.2 and 97.0 ppm, respectively, lying between the values of $\delta(^{119}Sn)$ for the neat starting components. We assume that in this system there is no formation of a donor–acceptor complex according to equation 2. A rapid equilibration, where the ions $[(Bu_3Sn)_3O]^+$ play the same role as H_3O^+ ions in aqueous solutions of acids, is probable (eq. 3).

$$(Bu_3Sn)_2O + Bu_3SnCl \rightleftharpoons \left[(Bu_3Sn)_3O\right]^+ + Cl^- \tag{3}$$

The chemical shifts $\delta(^{119}Sn)$ for compounds **9**–**10** as neat liquids and in $CDCl_3$ solutions (12.0–38.2 ppm) approach those of $Bu_3SnX \cdot D$ complexes, but are relatively far from those for alkoxides and phenoxides of tri-n-butyltin(IV) and their thio analogues (from 80 to 120 ppm) [11,17] with four-coordinate tin atom. The chemical shifts $\delta(^{119}Sn)$ of compounds **9**–**10** in pentadeuteriopyridine differ only slightly from those in $CDCl_3$ and in the neat liquids, and in hexamethylphosphortriamide they are again not as pronounced as for compounds **1**–**6**. We assume that all the data obtained can be accounted for in terms of the formation from compounds **9** and **10** of complexes with five-coordinate tin atoms involving chelate bonding of the substituents X (oxinate, diethyldithiocarbamate).

The chelate complexes **9** and **10** are relatively stable and show a low tendency to react with coordinating solvents. Such a reaction must be associated with the change of the chelate function of a ligand X from bidentate (X^2) to monodentate (X^1). The process can be represented as the displacement equilibrium 4.

$$Bu_3SnX^2 + D \rightleftharpoons Bu_3SnX^1 \cdot D \qquad (4)$$

This can also account for small changes in $\delta(^{119}Sn)$ for compounds **9** and **10** on going from $CDCl_3$ solutions to the neat liquids and especially to the solutions in coordinating solvents.

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

The coupling constants $^1J(^{119}Sn^{13}C)$, which are directly associated with the structure of organotin compounds [1], for compounds **1**–**6** as neat liquids and $CDCl_3$ solution exhibit here values of 326.7–386.7 Hz, typical of a quasitetrahedral arrangement of Bu_3SnX with four-coordinate tin atom [18]. The bonding of tin atom to the three n-butyl groups involves sp^3 hybrid orbitals of the tin atom and sp^3 hybrid orbitals of carbon atoms. The coupling constants $^1J(^{119}Sn^{13}C)$ for the compounds **7** and **8** in various solvents (with the exception of hexamethylphosphortriamide) lie within the same range. But the coupling constants $^1J(^{119}Sn^{13}C)$ of compounds **1**–**6** in coordinating solvents are higher (441.9–509.0 Hz), which correspond to a higher contribution of *s*-electrons to the bonding orbitals of the central tin atom. The ratio of the ^1J values of the $Bu_3SnX \cdot D$ complexes and free non-coordinated Bu_3SnX molecules of the compounds **1**–**6** varies in the range 1.17–1.47, i.e. near to the theoretical value of 1.33 for the ratio of *s*-character in sp^2 and sp^3 orbitals, respectively. Thus in $Bu_3SnX \cdot D$ complexes three n-butyl groups are bonded to central tin atom by sp^2 hybrid orbitals of the tin atom and sp^3 hybrid orbitals of carbon atoms, and the SnC_3 grouping has a planar geometry. The whole structure is formed by three n-butyl groups in an equatorial plane and the substituent X and monodentate ligand D in axial positions, thus giving *trans*-trigonal bipyramidal arrangement. The coupling constants $^1J(^{119}Sn^{13}C)$ for compounds **9** and **10** as neat liquids, in $CDCl_3$, and even in pentadeuteriopyridine, are slightly higher (350.2–395.5 Hz) than those for four-coordinate molecules **1**–**6** or **7**,**8**. In this case the n-butyl groups are bonded via sp^3 carbon orbitals to three sp^3 hybrid orbitals of the central tin atom, whose fourth orbital forms a three-centre bent bond with bonding orbitals of both donor atoms. Slightly higher values of ^1J for compounds **9** and **10** in hexamethylphosphortriamide (413.2 and 444.3 Hz, respectively) correspond to equilibrium 4.

The $^3J(^{119}Sn^{13}C)$ coupling constants of the compounds with sp^3 bonding orbitals at the central tin atom lie within the range 58.1–71.6 Hz, while for sp^2 hybrid orbitals they are in the range 73.2–80.6 Hz. The coupling constants $^2J(^{119}Sn^{13}C)$ and $^4J(^{119}Sn^{13}C)$ vary very little with a change of coordination; their values are relatively low. The ^4J constants for all the compounds are below 5 Hz.

^{13}C chemical shifts

The chemical shifts $\delta(^{13}C(1)–C(4))$ in most cases fall within the ranges typical of tri-n-butyltin(IV) compounds, and correspond to the values calculated from empirical relations [19]. For evaluation of the structure of compounds only the $\delta(^{13}C(1))$ chemical shifts are helpful; they are shifted downfield for compounds **1–6** in coordinating solvents relative to those for solutions in $CDCl_3$ or for the neat liquid. Compounds **7–9** in all the solvents exhibit $\delta(^{13}C)$ shifts close to those for the four-coordinate compounds **1–6**. It seems that, as with the triphenyltin(IV) compounds [1], the groups Bu_3Sn with planar geometry have $\delta(^{13}C(1))$ values different from those for the same groups with quasitetrahedral geometry and for the chelate complexes. The upfield shift of $\delta(^{13}C(1))$ for the planar groups can probably be associated with a decrease in the length and increase in the strength of the Sn–C bond, as evidenced by the results of structural analysis of complexes of five-coordinate triorganotin compounds with various donors or of crystalline polymers formed by autoassociation of the molecules [20]. We assume this fact also to be the cause of the substantial increase in the $^2J(SnH)$ coupling constant in the ^1H NMR spectra of *trans*-trigonal bipyramidal complexes of trialkyltin compounds relative to simple compounds with quasitetrahedral geometry [21]. The values of $\delta(^{13}C(COO))$ are noteworthy; they are shifted upfield in compounds **3–5** due to the formation of $Bu_3SnX \cdot D$ complexes, whereas the values of $\delta(^{13}C(i))$ in compounds **4** and **5** are shifted downfield as a result of the same reaction [3].

Discussion

Triorganotin compounds exist in solutions of various solvents either as simple quasitetrahedral molecules with four-coordinate central tin atoms or as complexes with trigonal bipyramidal geometry (*cis* or *trans*) at the five-coordinate central tin atom [1]. The structures can be distinguished for tri-n-butyltin(IV) compounds, as they can for triphenyltin(IV) compounds [1], by study of their ^{13}C and ^{119}Sn NMR parameters, especially of the $\delta(^{119}Sn)$ chemical shifts and the $^1J(^{119}Sn^{13}C)$ coupling constants. The range of chemical shifts $\delta(^{119}Sn)$ observed for tetrahedral arrangements of Bu_3SnX, 82.4–152.8 ppm, (compounds **1–8**) can be regarded as typical. If Bu_3SnX compounds with a substituent X bonded to tin atom via a carbon atom are excluded (we regard these compounds as tetraorganotin species), then $\delta(^{119}Sn)$ values falling outside the given range on the upfield side can be expected mainly for tri-n-butyltin(IV) compounds with tin–metal, tin–metalloid or tin–hydrogen bonds [21]. These compound cannot form complexes, and so they can be excluded from a discussion devoted to the distinguishing between coordination and configuration types. *trans*-Trigonal bipyramidal complexes $Bu_3SnX \cdot D$ show $\delta(^{119}Sn)$ values shifted upfield by ~ 100–190 ppm due to an increase in coordination number and electron density at the central tin atom. The observed range of $\delta(^{119}Sn)$ for the compounds under study (-60 to $+30$ ppm) is in a good agreement with those for other triorganotin complexes with monodentate ligands [21]. The observed coupling constants $^1J(^{119}Sn^{13}C)$ of the tetrahedral Bu_3SnX compounds (326.7–386.7 Hz) are typical of sp^3–sp^3 character of Sn–C bond in nonplanar Bu_3Sn grouping. A shift of ^1J for the *trans*-trigonal bipyramidal complexes into the region of 441.9–509.0 Hz is consistent with sp^2–sp^3 character in the Sn–C bond and a planar structure of Bu_3Sn grouping. The chelate complexes Bu_3SnX^2 exhibit $\delta(^{119}Sn)$ shifts close to those of *trans*-complexes because of the presence of a five coordinate tin atom, whereas their $^1J(^{119}Sn^{13}C)$ coupling constants approach those of simple tetrahedral molecules Bu_3SnX due to the sp^3–sp^3 character of Sn–C bond. Small differences in $\delta(^{13}C(1))$

are apparently associated with a geometry of Bu_3Sn grouping which is nearly the same in the tetrahedral molecules and chelate complexes, while for *trans*-trigonal bipyramidal complexes the $\delta(^{13}C(1))$ shifts are significantly higher.

All the above mentioned analogies between tri-n-butyl- and triphenyl-tin(IV) compounds are apparent from the correlation of NMR parameters $\delta(^{119}Sn)$ and $^1J(^{119}Sn^{13}C)$ shown in Figs. 1 and 2. For these figures we used the NMR data for triphenyltin(IV) compound from our previous papers [1–3,22]. From Fig. 1 it can be seen that the compounds with different coordination form two separate sets. The values of coupling constants $^1J(^{119}Sn^{13}C)$ for different *s*-orbital contributions to the hybrid orbitals of the central tin atom similarly fall into two sets. The relationship of the chelate complexes **9** and **10** to the other complexes in terms of the $\delta(^{119}Sn)$ values, and to simple tetrahedral compounds in terms of the $^1J(^{119}Sn^{13}C)$ values, is indicated by the full circles in the relevant figures. The relations in Figs. 1. and 2 are

$$[\delta(^{119}Sn)(Bu_3Sn)] = (0.89 \pm 0.05)[\delta(^{119}Sn)(Ph_3Sn)] + (201.68 \pm 9.45) \qquad (N = 16,\ r = 0.980) \qquad (5)$$

$$[^1J(^{119}Sn^{13}C)(Bu_3Sn)] = (0.60 \pm 0.02)[^1J(^{119}Sn^{13}C)(Ph_3Sn)] - (18.12 \pm 18.42) \qquad (N = 16,\ r = 0.988) \qquad (6)$$

The slopes in both the correlations are slightly lower than the theoretical values of 1.00 and 0.75, respectively.

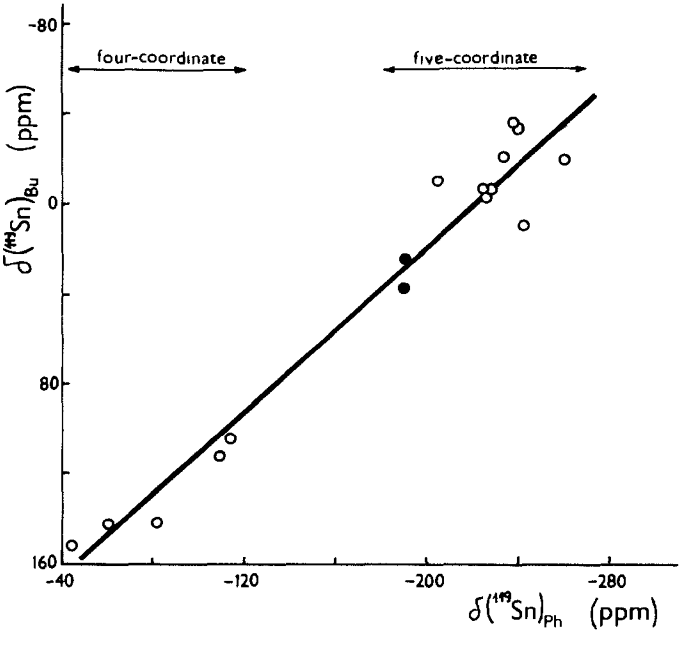

Fig. 1. Correlation of ^{119}Sn chemical shifts in tri-n-butyltin(IV) compounds with ^{119}Sn chemical shifts in triphenyltin(IV) analogues. Compound **9** and **10** are denoted by full circles.

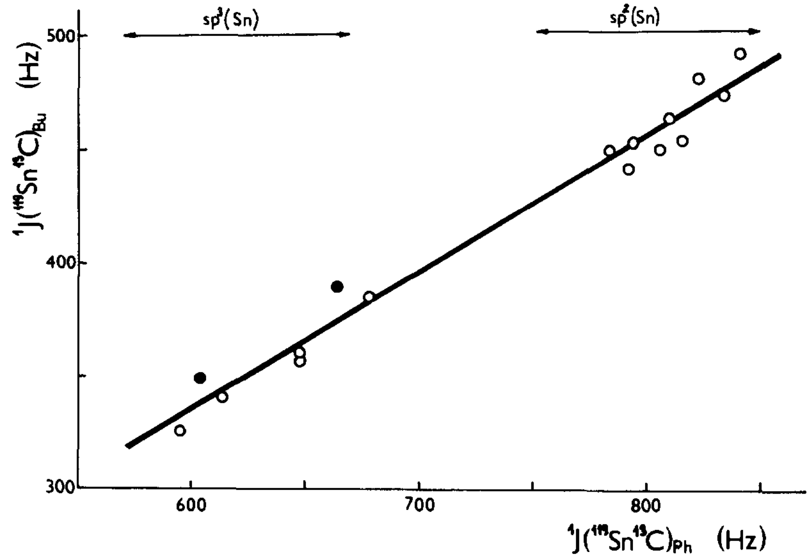

Fig. 2. Correlation of $^1J(^{119}Sn^{13}C)$ coupling constants in tri-n-butyltin(IV) compounds with $^1J(^{119}Sn^{13}C)$ coupling constants in triphenyltin(IV) analogues. Compounds **9** and **10** are denoted by full circles.

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