^{13}C AND ^{119}Sn NMR SPECTRA OF DIPHENYL- AND DIBENZYLTIN(IV) COMPOUNDS AND THEIR COMPLEXES

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^{13}C and ^{119}Sn NMR spectra of diphenyl- and dibenzyltin(IV) compounds have been studied in solutions of coordinating and non-coordinating solvents. Regions of values of the $\delta(^{119}$Sn) chemical shifts have been determined which characterize individual types of coordination of the central tin atom. The values of ^{13}C NMR spectral parameters, the $\delta(^{13}$C) chemical shifts and $^nJ(^{119}$Sn, ^{13}C) coupling constants, have been used to describe the real shapes of coordination sphere of the central tin atom and to discuss the internal structure of the organic substituents and of the nature of their bonding linkage to the tin atom.

Our previous communications[1-4] showed the usefulness of the knowledge of ^{13}C and ^{119}Sn NMR spectral parameters of triorganotin(IV) compounds for a qualitative or semiquantitative description of structure of their particles in solutions of various types of solvents, and the paper[5] also showed the interdependence of these parameters of various triorganotin(IV) compounds with different types of organic substituents at the tin atom. In the communications[6,7] we extended the findings about the interdependence of the $\delta(^{119}$Sn) and $\delta(^{13}$C) parameters with the coordination of the central tin atom, and of the $^nJ(^{119}$Sn, ^{13}C) coupling constants with the geometry of arrangement of organic substituents near the central tin atom, also to dibutyl- and divinyltin(IV) compounds and their complexes.

The present communication will summarize the results of our investigation of ^{13}C and ^{119}Sn NMR spectra of other two types of diorganotin(IV) compounds, viz. diphenyl- and dibenzyltin(IV) compounds R_2SnX_2 and their tetraethylammonium halogenocomplexes $[Et_4N]^+[R_2SnX_3]^-$ (see Scheme 1) in solutions of both coordinating (hexadeuteriodimethyl sulfoxide, pentadeuteriopyridine, trideuterionitromethane) and non-coordinating solvents (deuteriochloroform).

The aim of the present communication was (i) to delimit the regions of values of $\delta(^{119}$Sn) and (if possible) also $\delta(^{13}$C) chemical shifts characterizing the individual types of coordination of the central tin atom, (ii) to describe the real shapes of the coordination polyhedra in close vicinity of the tin atom on the basis of the $^nJ(^{119}$Sn,

[13]C) coupling constants, (iii) to add more details to the description of internal structure of the organic substituents and nature of the bonding linkage Sn—C.

IA - IXA   IB - IXB

XA and XIA   XB
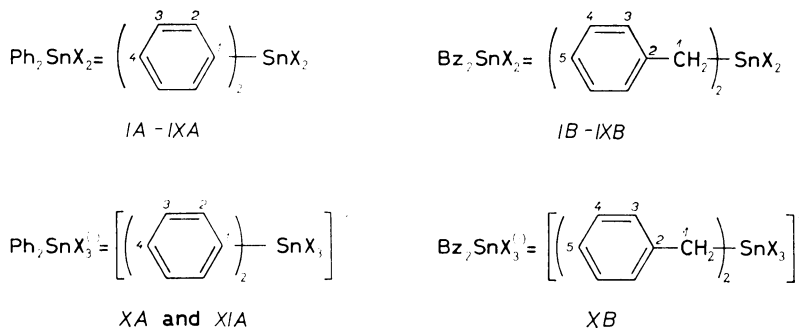
X = Cl (*I* and *X*), Br (*II* and *XI*), I (*III*), CH$_3$COO (*IV*), C$_6$H$_5$COO (*V*), oxin = 8-quinolinolate C$_{10}$H$_7$NO (*VI*), toxin = 8-quinolinethiolate C$_{10}$H$_7$NS (*VII*), edtc = N,N-diethyldithiocarbamate (C$_2$H$_5$)$_2$NCS$_2$ (*VIII*), acac = 2,4-pentanedionate (CH$_3$CO)$_2$CH (*IX*)

SCHEME 1

EXPERIMENTAL

Most compounds studied in the present communication were prepared according to known procedures[8–16]. Compounds *XIA*, *IXB*, and *XB* which, as far as we know, have not been described yet were prepared according to the procedures given in literature[11,13] for analogous organotin(IV) compounds. Elemental analyses and melting points of these substances are summarized in Table I.

The ^{13}C and ^{119}Sn NMR spectra were measured at 25·047 and 37·14 MHz, respectively, using a JNM-FX 100 apparatus at 300 K. The solutions used were c. 5% to 25% (w/w) or saturated (if the substances were less soluble). The δ([119]Sn) chemical shifts are related to external tetramethylstannane, the δ(^{13}C) chemical shifts are related to the respective signal of solvent and transferred to the δ scale: deuteriochloroform 77·00 ppm, hexadeuteriodimethyl sulfoxide 39·60 ppm, pentadeuteriopyridine 149·00 ppm (C(2)). Positive values of the chemical shifts denote upfield shifts with respect to the standard. More detailed descriptions of experimental conditions are given in our previous papers[1,2].

RESULTS AND DISCUSSION

The ^{13}C and ^{119}Sn NMR parameters are listed in Tables II and III for the diphenyl- and dibenzyltin(IV) compounds studied, respectively.

The δ([119]Sn) Chemical Shifts

The values of δ([119]Sn) chemical shifts of the diphenyltin(IV) compounds (Table II)

and dibenzyltin(IV) compounds (Table III) measured at about the same experimental conditions exhibit a good mutual linear correlation and, in addition, a **linear** correlation with the $\delta(^{119}Sn)$ values found for bis-(1-butyl)tin(IV) compounds[6] as it can be seen from Fig. 1. The respective linear correlation can be expressed in the following analytical form:

$$\delta(^{119}Sn)\left(R_2^{(1)}Sn\right) = a\,\delta(^{119}Sn)\left(R_2^{(2)}Sn\right) + b\,, \qquad (1)$$

TABLE I

Analytical and physical data of compounds *XIA*, *IXB*, and *XB*

Compound	Calculated/Found, %				M.p., °C
	C	H	Sn	others	
XIA	37·37	4·70	18·46	N 2·18	135—136
	37·11	4·83	18·32	2·24	
				Br 37·29	
				36·98	
IXB	57·75	5·65	23·78		62—64
	57·88	5·36	23·76		
XB	49·16	6·38	22·08	N 2·61	59—62
	49·28	6·36	21·92	2·56	
				Cl 19·78	
				19·84	
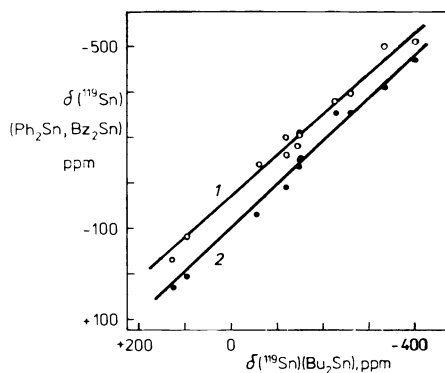
FIG. 1

The linear correlations $\delta(^{119}Sn)(Ph_2Sn) \sim \delta(^{119}Sn)(Bu_2Sn)$ (*1*) and $\delta(^{119}Sn)(Bz_2Sn) \sim \delta(^{119}Sn)(Bu_2Sn)$ (*2*)

TABLE II

The ^{13}C and ^{119}Sn NMR spectral parameters of diphenyltin(IV) compounds

Compound[a]	δ(^{119}Sn)[b]	δ(^{13}C)/(^nJ(^{119}Sn, ^{13}C), Hz)				The other δ(^{13}C) values
		C(1)	C(2)	C(3)	C(4)	
IA^c	−26·7 (−27·0)	136·75 (786·0)	134·90 (63·5)	129·63 (86·7)	131·78 (17·0)	
IA^d	−77·7 (−59·1)	139·46 (825·2)	136·34 (64·7)	131·03 (89·1)	133·13 (18·4)	
$IA^{e,f,g}$	−405·1 [h]	155·0 (1 548·7)	134·9 (70·6)	127·3 (125·0)	127·7 (23·5)	
IIA^c	−71·8 (−71·7)	137·14 (727·5)	134·75 (63·5)	129·49 (83·0)	131·54 (17·1)	
IIA^d	−90·9 (−85·7)	139·22 (750·8)	136·15 (64·7)	131·03 (86·0)	133·03 (18·04)	
$IIIA^c$	−242·1 (−241·6)	136·07 (636·0)	134·66 (62·3)	129·20 (80·6)	131·19 (18·0)	
$IIIA^d$	−244·4 [h]	137·76 [h]	135·98 (62·3)	130·74 (80·6)	132·83 (17·0)	
IVA^c	−302·5 (−302·8)	138·16 (996·1)	135·44 (65·9)	128·95 (95·2)	130·66 (19·5)	181·93 (COO), 20·03 (CH$_3$)

VA^c	−306·1 (−306·6)	138·75 (1 012·0)	135·73 (65·9)	129·10 (96·4)	130·81 h	176·08 (COO), 130·17 (i), 130·81 (o), 128·32 (m), 133·53 (p).
$VIA^{c,i}$	−393·7 (−394·2)	149·66 (937·6)	135·06 (54·1)	127·99 (80·2)	128·11 (16·3)	see ref.[9]
$VIIA^{c,j}$	−273·6 h	154·49 (728·6)	134·39 (55·6)	127·84 (74·7)	127·65 (17·7)	see ref.[10]
$VIIIA^c$	−501·0 (−502·3)	151·0 (806·0)	133·98 (61·5)	127·90 (84·1)	128·07 (17·6)	197·69 (CSS), 50·15 (CH_2), 11·95 (CH_3)
IXA^c	−512·3 (−512·3)	149·19 (1 040·4)	135·15 (57·1)	127·66 (87·1)	128·07 (17·6)	193·01 (CO), 100·99 (CH), 27·62 (CH_3)
XA^d	−257·3 (−256·8)	150·14 (1 074·2)	136·98 (68·4)	129·23 (97·6)	130·54 (21·0)	53·30 (CH_2), 7·73 (CH_3)
XIA^d	−301·2 (−304·0)	150·77 (997·6)	136·25 (68·5)	129·28 (99·4)	130·56 (20·7)	53·53 (CH_2), 7·80 (CH_3)

[a] See Scheme 1. [b] The first date concerns the concentration of c. 5% (w/w), that in parenthesis concerns c. 25% (w/w). [c] C^2HCl_3. [d] $C^2H_3NO_2$. [e] $(C^2H_3)_2SO$. [f] See ref.[17]. [g] $\delta(^{119}Sn)$: −392·1 ($C_5{}^2H_5N$), −389·5 ($C^2HCl_3 : C_5{}^2H_5N = 1:1$), −388·9 ($C^2HCl_3 : C_5{}^2H_5N = 2:1$). [h] Not determined. [i] See ref.[9]. [j] See ref.[10].

TABLE III
The ^{13}C and ^{119}Sn NMR spectral parameters of the dibenzyltin(IV) compounds

Compound[a]	$\delta(^{119}\text{Sn})^b$ $(^2(J^{119}\text{Sn},^1\text{H}), \text{Hz})$	$\delta(^{13}\text{C})/(^nJ(^{119}\text{Sn},^{13}\text{C}), \text{Hz})$					The other $\delta(^{13}\text{C})$ values
		C(1)	C(2)	C(3)	C(4)	C(5)	
IB[c]	32·2 (79·6)	32·5 (390·6)	134·61 (56·2)	128·32 (46·4)	129·15 (25·7)	126·32 (31·8)	
IB[d]	−361·2 (144·5)	49·15 (922·9)	140·09 (90·3)	129·71 (58·6)	127·67 (36·0)	124·60 (42·7)	
IIB[c]	−0·5 (73·7)	32·95 (353·1)	135·03 (60·1)	128·13 (44·0)	128·95 (26·4)	126·08 (31·7)	
IIB[d]	−371·1 (140·6)	52·08 (888·7)	139·75 (91·6)	129·71 (60·4)	127·86 (37·8)	124·94 (44·0)	
IIIB[c]	−130·8 (63·0)	31·97 (296·6)	136·36 (58·6)	127·98 (41·6)	128·90 (26·9)	125·88 (31·7)	
IIIB[d]	−414·1 (136·7)	48·91 (872·8)	138·88 (89·1)	129·81 (58·6)	128·20 (37·8)	125·38 (43·9)	
IVB[c]	−247·5 (92·3)	31·38 (548·1)	135·48 (72·0)	128·10 (45·2)	128·10 (25·6)	125·15 (30·5)	181·3 (COO), 19·69 (CH$_3$)

IVB^d	-445.2 (141.1)	38.72 (908.5)	139.46 (83.5)	128.87 (54.3)	127.53 (33.7)	124.14 (39.6)	179.3 (COO), 10.65 (CH$_3$).
VB^c	-252.5 (94.2)	32.36 (556.6)	135.73 (74.5)	128.27 (45.2)	128.27 (25.6)	125.25 (31.1)	176.0 (COO), 129.49 (i), 130.32 (o), 126.03 (m), 133.05 (p)
VB^d	-448.7 (141.1)	39.11 (910.6)	139.36 (84.2)	128.89 (55.0)	127.52 (34.2)	124.11 (39.0)	174.3 (COO), 136.76 (i), 129.57 (o), 128.30 (m), 132.39 (p)
$VIB^{c,e}$	-355.2 (90.9)	33.19 (543.2)	141.58 (62.1)	127.68 (38.4)	127.30 (23.5)	122.56 (27.5)	see ref.[9]
$VIIB^{c,f}$	-235.2 (71.6)	41.17 (444.2)	141.69 (62.6)	127.36 (39.1)	127.17 (26.1)	122.79 (31.0)	see ref.[10]
$VIIIB^c$	-407.2 (92.8)	41.52 (537.2)	139.24 (78.1)	129.03 (50.0)	127.34 (30.4)	124.52 (36.0)	197.96 (CSS), 47.19 (CH$_2$), 11.89 (CH$_3$)
IXB^c	-467.9 (116.7)	33.91 (739.7)	141.06 (68.4)	128.39 (46.4)	127.25 (28.1)	122.94 (33.0)	191.82 (CO), 27.32 (CH$_3$), 100.26 (CH)
XB^g	-188.2 (99.1)	43.89 (608.0)	139.02 (77.6)	129.52 (51.2)	128.45 (28.1)	125.43 (34.2)	52.71 (NCH$_2$), 7.09 (CH$_3$)

[a] See Scheme 1. [b] C. 20% solutions (w/w). [c] C^2HCl_3. [d] $(C^2H_3)_2SO$. [e] See ref.[9] [f] See ref.[10] [g] $C^2H_3NO_2$.

where $R_2^{(1)}Sn$ and $R_2^{(2)}Sn$ represent pairs of diorganotin(IV) compounds with different organic substituents — $R^{(1)}$ = phenyl (Ph) or benzyl (Bz), $R^{(2)}$ = benzyl or 1-butyl (Bu). The values of slopes (a) and intercepts (b) of the linear correlations (1) are summarized in Table IV.

From the mutual interdependence of the chemical shifts expressed by formula (1) and from the limiting values of the $\delta(^{119}Sn)$ chemical shifts of bis(1-butyl)tin(IV) compounds for various coordination types (various values of the coordination number) of the central tin atom[6] it is possible also to predict (with a high degree of probability) the regions of the $\delta(^{119}Sn)$ chemical shifts typical of the corresponding types of coordination of diphenyl- and dibenzyltin(IV) compounds (Table V).

Justifiability of the thus delimited regions of the $\delta(^{119}Sn)$ chemical shifts of diphenyltin(IV) compounds (the dibenzyl analogues have been studied only sporadically up to now) is confirmed by many literature data. The $\delta(^{119}Sn)$ values from +30 to −220 ppm are exhibited, e.g., by the monomeric pseudotetrahedral diphenyltin(IV)

TABLE IV

The values of slope (a) and intercept (b) in the linear correlation of Eq. (1)

$R^{(1)}$	$R^{(2)}$	a	b	N^a	r^b
Phenyl	benzyl	0.98 ± 0.05	-69.24 ± 13.66	10	0.988
Phenyl	1-butyl[c]	0.95 ± 0.05	-161.88 ± 9.63	12	0.988
Benzyl	1-butyl[c]	1.00 ± 0.06	-91.17 ± 24.58	11	0.987

[a] Number of pairs. [b] The correlation coefficient. [c] See ref.[6].

TABLE V

The regions of characteristic $\delta(^{119}Sn)$ values (ppm) of the diphenyl- and dibenzyltin(IV) compound studied

Compounds	$\delta(^{119}Sn)$ for the coordination number of central tin atom			
	4	5	6	7
Diphenyltin(IV)	+30 to −220	−250 to −340	−360 to −540	−600 and higher
Dibenzyltin(IV)	+110 to −150	−180 to −280	−300 to −490	−540 and higher
Bis(1-butyl)tin(IV)[a]	+200 to −60	−90 to −190	−210 to −400	−450 and higher

[a] See ref.[6].

compounds $Ph_2Sn(ER)_2$, $(Ph_2SnX)_2CH_2$, and $(Ph_2SnER)_2CH_2$ $(X = Cl, Br, or I;$ $E = O, S, Se, or Te)$ and trimeric particles $(Ph_2SnS)_3$ (refs[18,19]). The particles with trigonally bipyramidal environment of the tin atom such as Ph_2SnXY $(X = $ a halogen atom, $Y = $ a bidentate ligand such as oxinate, xanthate, dithiocarbamate, carboxylate etc.)[20], complexes $Ph_2SnX_2.D$ $(D = $ a molecule of triorganophosphine oxide)[21,22] and dimers $(Ph_2SnOCOR)_2$ (ref.[23]) exhibit $\delta(^{119}Sn)$ values which cover almost the whole region delimited in the present paper for diphenlytin(IV) compounds with the coordination number of the tin atom equal to five. The $\delta(^{119}Sn)$ chemical shifts of the complexes Ph_2SnY_2 $(Y = $ bidentate ligand $-$ see above) mostly vary about -400 to -500 ppm (refs[18,24]), the only exceptions being some compounds with anisobidentate function of a two donor ligand[18,25] (see below). The compound $[Ph_2Sn(pan)(acac)]$ containing one tridentate (pan $= $ 1-(2-pyridyl-azo)-2-naphtholate) and one bidentate ligand (acac) in a heptacoordinated environment of the central tin atom shows the chemical shift $\delta(^{119}Sn) = -602$ ppm in deuteriochloroform solution[26].

The $\delta(^{119}Sn)$ chemical shift values of the diphenyl- and dibenzyltin(IV) compounds studied in the present paper vary within broad limits and cover practically the whole region delimited for these diorganotin(IV) compounds with the coordination number of the central tin atom equal to four, five, and six.

Solutions of diphenyl- $(IA-IIIA)$ and dibenzyltin(IV) halides $(IB-IIIB)$ in non--coordinating solvents (deuteriochloroform) show almost concentration-independent values of the $\delta(^{119}Sn)$ chemical shifts from the regions characterizing the respective tetracoordinated compounds. Their pseudotetrahedral molecules in deuteriochloroform solution (and similarly also in crystalline state[27]) are more or less isolated without any distinct tendency to association. The marked upfield shift in the $\delta(^{119}Sn)$ values of the solutions of the same compounds in coordinating solvents (hexadeuteriodimethyl sulfoxide or pentadeuteriopyridine) is due to the coordination change by formation of complexes with two solvent molecules according to the equilibrium reaction

$$R_2SnX_2 + 2D \rightleftharpoons R_2SnX_2.2D \qquad (A)$$
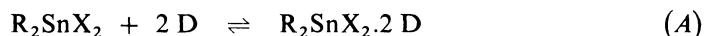
$(X = Cl, Br, or I; D = $ a molecule of coordinating solvent; $R = $ Ph or Bz). The mutually near values of the chemical shifts $\delta(^{119}Sn)$ of solutions of compound IA in various coordinating solvents $((C^2H_3)_2SO, C_5{}^2H_5N$ and its mixtures with C^2HCl_3, Table II) on the one hand, and those of compounds with various polar groups $(IB, IIB, $ and $IIIB)$ in the same solvent $((C^2H_3)_2SO)$ on the other hand, indicate that the complex formation process of $R_2SnX_2.2D$ in these solvents is completely shifted to the right-hand side of Eq. (A). On the contrary, an only partial formation of the complexes according to Eq. (A) is indicated by the $\delta(^{119}Sn)$ values and their concentration changes for solutions of compounds IA, IIA, and $IIIA$ in the medium of weakly coordinating solvent $-$ trideuterionitromethane (Table II).

Diphenyl- and dibenzyltin(IV) oxinates (*VIA* and *VIB*), N,N-diethyldithiocarbamates (*VIIIA* and *VIIIB*), and 2,4-pentanedionates (*IXA* and *IXB*) form hexacoordinated pseudooctahedral chelate complexes (bidentate function of the oxin, edtc, and acac ligands) even in the medium of non-coordinating deuteriochloroform. The anions $R_2SnX_3^-$ of the complexes *XA*, *XIA*, and *XB* are trigonally bipyramidal (the coordination number of tin is equal to five). Special attention should be paid to the carboxylates (*IVA*, *IVB*, *VA*, *VB*) and 8-quinolinethiolates (*VIIA*, *VIIB*) whose $\delta(^{119}Sn)$ values in deuteriochloroform solutions correspond to an apparently pentacoordinated central tin atom, in reality, however, they are hexacoordinated complexes with anisobidentate function of carboxylic and 8-quinolinethiolate groups (a 4 + 2 coordination), which we discussed in detail in our earlier papers[10,28]. The $\delta(^{119}Sn)$ values of the carboxylates *IVB* and *VB* in hexadeuterodimethyl sulfoxide indicate the complex formation according to Eq. (*A*); the complexes contain monodentate carboxylic groups[7,28].

The $^nJ(^{119}Sn, {}^{13}C)$ and $^2J(^{119}Sn, {}^1H)$ Coupling Constants

It is known[29] that the absolute values of coupling constants $|^1J(^{119}Sn, {}^{13}C)|$ can provide information about magnitudes of average C—Sn—C angles (Θ) in particles of organotin(IV) compounds. Recently we have found[29] the linear dependence of $|^1J(^{119}Sn, {}^{13}C)| \sim \Theta$ in the form (2) for a group of tetra-, tri-, and diphenyltin(IV) compounds.

$$|^1J(^{119}Sn, {}^{13}C)| = (15 \cdot 56 \pm 0 \cdot 84)\,\Theta - (1\,160 \pm 101) \tag{2}$$

Table VI gives the Θ values calculated from this relation for diphenyltin(IV) compounds. From magnitudes of the Θ angles it is seen that none of the particles of the diphenyltin(IV) compounds studied has an ideal shape. The deformations of real shapes of coordination polyhedra are due to operation of electronic and steric effects of heterogeneous organic substituents and polar groups and, in the case of complexes, also different donor abilities of the individual ligands. Out of the tetracoordinated compounds the ideal tetrahedron ($\Theta = 109 \cdot 5°$) is most nearly attained by the Ph_2SnI_2 molecule ($\Theta = 115°$), and the Θ angle is distinctly increased with increasing electronegativity of halogen atoms. The particles of pentacoordinated anions $Ph_2SnX_3^-$ (compounds *XA* and *XIA*) in ideal case should have the shape of *cis*-trigonal bipyramid[31]. The Θ angle (~ 144 and $138°$, respectively), however, is distinctly greater than the ideal value of $120°$. Out of the complexes with the coordination number of the central tin atom equal to six the complex Ph_2SnCl_2. .2 $(C^2H_3)_2SO$ ($\Theta \sim 174$ according to Eq. (2), being $169 \cdot 7°$ in crystalline state[32]) stands nearest to the ideal case of trans-octahedral complex ($\Theta = 180°$). The shapes of coordination polyhedra of the other hexacoordinated complex diphenyltin(IV)

compounds can be denoted, according to the magnitude of Θ angle, as deformed *cis*-octahedra (compounds *VIIA* and *VIIIA*) or trapezoidal bipyramids (skew)[33] (compounds *IVA, VA, VIA, IXA*).

TABLE VI

The C–Sn–C angles (Θ) and substituent constants σ_I and σ_{R^0} of the diphenyl- and dibenzyltin(IV) compounds investigated

Compound[a]	$\Theta, °^b$	σ_I^c	$\sigma_{R^0}^d$	Compound[a]	σ_I^c	$\sigma_{R^0}^d$
IA[e]	125[h]	0·48	0·06	*IB*[e]	0·24	−0·15
IA[f]	174[i]	−0·06	−0·01	*IB*[f]	−0·07	−0·15
IIA[e]	121	0·44	0·06	*IIB*[e]	0·20	−0·15
IIIA[e]	115	0·38	0·05	*IIIB*[e]	0·18	−0·15
IVA[e]	138	0·32	0·04	*IVB*[e]	0·02	−0·15
VA[e]	140	0·35	0·04	*VB*[e]	0·05	−0·15
VIA[e]	134	0·07	−0·02	*VIB*[e]	−0·19	−0·23
VIIA[e]	121	0·03	−0·04	*VIIB*[e]	−0·21	−0·21
VIIIA[e]	126[j]	0·06	−0·02	*VIIIB*[e]	−0·13	−0·14
IXA[e]	141	0·01	−0·01	*IXB*[e]	−0·23	−0·15
XA[g]	144	0·36	0·03	*XB*[g]	0·09	−0·15
XIA[g]	138	0·37	0·03			

[a] See Scheme 1. [b] $\pm 12°$, according to Eq. (2). [c] According to the equation ^{13}C SCS(*para*) = = $4·73\sigma_I + 20·98\sigma_{R^0}$ (ref.[36]), $\delta(^{13}C)$(benzene) = 128·25. [d] According to Eq.: $\delta(^{13}C)$(*para*) − $\delta(^{13}C)$(*meta*) = $23·9\sigma_{R^0} + 0·68$ (ref.[37]). [e-g] Solvents: [e] C^2HCl_3, [f] $(C^2H_3)_2SO$, [g] $C^2H_3NO_2$. [h-j] In the crystalline state: [h] 125·7° (ref.[27]), [i] 169·7° (ref.[31]), [j] 101·4° (ref.[30]).
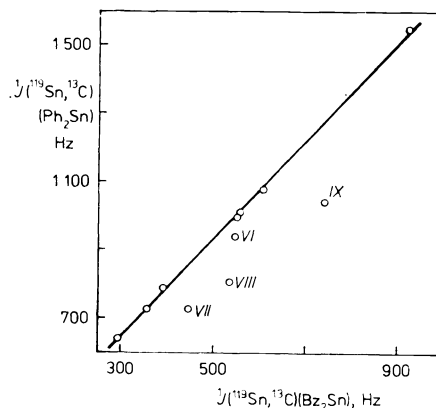
FIG. 2

The linear correlation $^1J(^{119}Sn, ^{13}C)$ . . $(Ph_2Sn) \sim \, ^1J(^{119}Sn, ^{13}C)\,(Bz_2Sn)$

A relation of the type (2) cannot be formulated at present for benzyltin(IV)com-
pounds which are generally less studied. However, a certain conclusion about the
geometry around the tin atom of the benzyltin(IV) compounds studied can be made
from comparison of the $^1J(^{119}Sn, {}^{13}C)$ values of dibenzyl- and diphenyltin(IV)
compounds. From Fig. 2 it is seen that these values show mutual linear correlation,
wherefrom the only deviating complexes are $R_2Sn(oxin)_2$, $R_2Sn(txin)_2$, $R_2Sn(acac)_2$,
and $R_2Sn(edtc)_2$ (R = phenyl or benzyl). It can be presumed that the deformation
of coordination polyhedra of benzyl- and phenyltin(IV) compounds (except for the
dichelates mentioned) will not be mutually too different, however, the Θ angles of
dibenzyltin(IV) dichelates will be somewhat greater than those of analogous diphenyl-
tin(IV) compounds. The same conclusions can also be made from the $^2J(^{119}Sn, {}^1H)$
values (Table III), since they show excellent correlation with the $^1J(^{119}Sn, {}^{13}C)$
values according to Eq. (3).

$$^2J(^{119}Sn, {}^1H) = (0.13 \pm 0.00)\,{}^1J(^{119}Sn, {}^{13}C) + (22.90 \pm 2.96) \qquad (3)$$

$$N = 15, \quad r = 0.993$$

Nonzero values of the $^5J(^{119}Sn, {}^{13}C)$ coupling constants were found with all the
dibenzyltin(IV) compounds studied. In addition, these values are higher than those
of the $^4J(^{119}Sn, {}^{13}C)$ constants in all the cases. Hence in all the particles of the
benzyltin(IV) compounds studied we shall encounter conformers with nonplanar
arrangement of the $Sn—CH_2—C_6H_5$ fragment which fulfil the basic geometrical
condition for hyperconjugation bonding connection of the polarized σ bond Sn—C
with the π electron system of aromatic nucleus[3,34].

The $\delta(^{13}C)$ Chemical Shifts

The following effects ((i)−(iii)) can be exerted[35] upon the phenyl groups of the
diphenyl- and dibenzyltin(IV) compounds by the substituents R^1 and R^2, respecti-
vely, these substituents being − for our purpose − the residues of molecules, ions,
or complexes of diphenyl- and dibenzyltin(IV) compounds after removal of one
phenyl group.

(i) The donor or acceptor inductive effects of the substituents R^1 and R^2. (ii)
A partial transfer of π electron density of phenyl group to the outer d-orbitals of the
tin atom (the so-called $(p–d)$ π conjugation) where the R^1 fragment acts as an electron
acceptor. (iii) The so-called σ–π conjugation (hyperconjugation), i.e. interaction of
polarized bonds of the tin atom and some of its bonding partners with the π electron
system of aromatic ring. Generally, this type of conjugation is considered the cause
of electron-donor properties of the substituents R^1 and R^2, however, more generally
it can be considered to be an alternative of the $(p–d)$ π conjugation concept.

Information about the extent of operation of the individual substituent effect in the diphenyl- and dibenzyltin(IV) compounds studied can be obtained from the $\delta(^{13}C)$ chemical shift values of carbon atoms in the phenyl and benzyl groups and the therefrom calculated values of substituent constants σ_I and σ_{R^0} (Table VI) (refs[36,37]).

From Table VI it is obvious that the R^1 substituent affects the phenyl ring predominantly by its inductive effects. The R^1 substituents derived from the coordinatively unsaturated tetra- and pentacoordinated diphenyltin(IV) compounds act on the phenyl ring as relatively strong electron acceptors distinctly depending on the nature of polar groups bound to the tin atom (σ_I from 0·32 to 0·48). The presence of ligands in the saturated coordination sphere of the tin atom in hexacoordinated diphenyltin-(IV) compounds increases the electron density at this central atom, due to which the electron-acceptor abilities of the respective R^1 substituents markedly decrease (σ_I from $-0·06$ to $+0·07$). The resonance constants σ_{R^0} of the R^1 substituents generally are very small. Hence from the results of ^{13}C NMR spectra it cannot be reliably decided whether the two alternatives of conjugative connection in the diphenyltin(IV) compounds are mutually compensated or whether they make themselves felt at all. However, it should be noticed that in all the diphenyltin(IV) compounds studied an upfield shift in the $\delta(^{13}C)$ value at the C(1) atom is connected with downfield shifts at the C(3) and C(4) atoms and vice versa. Relatively the smallest effect of structural changes is observed on the $\delta(^{13}C)$ values of C(2) atom. According to this fact it is possible to ascribe the dominant role of the inductive effect of R^1 substituent to the π-inductive mechanism[38].

The metallomethyl substituents R^2 derived from the dibenzyltin(IV) compounds act on the phenyl ring as both resonance donors and (according to composition) inductive donors or acceptors. The resonance-donor ability of the R^2 substituents is not much influenced by the composition of dibenzyltin(IV) compounds, perhaps a certain role is played by the mutual position of organic and polar groups and donor atoms of ligands. According to expectation (the presence of a methylene group between the tin atom and phenyl nucleus) the inductive electron-acceptor action of the R^2 substituents is markedly weakened as compared with that of R^1. The R^2 substituents derived from coordinatively saturated hexacoordinated dibenzyltin(IV) compounds behave as distinct donors.

The resonance-donor properties of the R^2 substituents confirm the existence of conjugative bonding connection of the polarized σ bond Sn—C with the π electron system of aromatic ring. This connection, inter alia, also weakens the Sn—C bond in the Sn—C(H$_2$)—C$_6$H$_5$ fragment in favour of the C(H$_2$)—phenyl bond, which makes itself felt in lower values of the $^1J(^{119}Sn, ^{13}C)$ constants of the benzyltin(IV) compounds not only in comparison with the diphenyltin(IV) compounds but also in comparison with other diorganotin(IV) compounds having the same shapes of the

hybridized orbitals at the tin and C(1) atoms, e.g. with the bis(1-butyl)tin(IV) compounds[6].

The values of $\delta(^{13}C)$ chemical shift at C(1) atom in both series of the compounds studied (Tables II and III) depend on the coordination of the central tin atom, hence they can be utilized for prognoses concerning structure of these diorganotin(IV) compounds. However, their information value is lower as compared with that of the $\delta(^{119}Sn)$ values due to the lower range of regions characterizing the individual coordination numbers of the tin atom (the $\delta(^{13}C(1))$ difference for the tetra- and hexacoordinated compounds does not exceed 20 ppm) and due to the partial overlap of these regions.

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