

^{13}C AND ^{119}Sn NMR EVIDENCE OF THE PRESENCE AND EXTENT OF σ - π CONJUGATION IN SOME BENZYL TIN COMPOUNDS AND THEIR COMPLEXES

Jaroslav HOLEČEK^a, Antonín LYČKA^b, Karel HANDLÍŘ^a and Milan NÁDVORNÍK^a

^a Department of General and Inorganic Chemistry

Institute of Chemical Technology, 532 10 Pardubice and

^b Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví

Received May 29th, 1987

Dedicated to Prof. M. Večeřa on the occasion of his 65th birthday.

The ^{13}C and ^{119}Sn NMR spectroscopy has been used to study the compounds types $(\text{C}_6\text{H}_5\text{CH}_2)_{4-n}\text{Sn}(\text{CH}_3)_n$ and $(\text{C}_6\text{H}_5\text{CH}_2)_{4-n}\text{SnCl}_n$ ($n = 0-3$) in media of non-coordinating (deuteriochloroform) and coordinating (hexadeuteriodimethyl sulphoxide) solvents. The analysis of the NMR data has confirmed the presence and established the relative extent of participation of the σ - π conjugative connection of the polarized $\sigma(\text{Sn}-\text{C})$ bond with the adjacent π electronic system of the aromatic ring in the $\text{Sn}-\text{CH}_2-\text{C}_6\text{H}_5$ grouping. The extent of σ - π conjugation decreases with decreasing number of methyl groups in the compounds $(\text{C}_6\text{H}_5\text{CH}_2)_{4-n}\text{Sn}(\text{CH}_3)_n$ and with increasing number of chlorine atoms in the compounds $(\text{C}_6\text{H}_5\text{CH}_2)_{4-n}\text{SnCl}_n$ and with increasing coordination number of the central tin atom in the complexes of the compounds $(\text{C}_6\text{H}_5\text{CH}_2)_{4-n}\text{SnCl}_n \cdot x(\text{C}^2\text{H}_5)_2\text{SO}$.

The problems of the presence and extent of conjugative connection between a $\sigma(\text{Sn}-\text{C})$ bond and adjacent π electronic system of various metallomethylaromatics, -alkenes, and -alkynes can be studied – beside other chemical and physical methods – advantageously by means of multinuclear magnetic resonance. A number of monobenzyl- and monoallyltin(IV) compounds and their derivatives carrying various organic groups at both the tin atom and the carbon atoms of benzyl or allyl groups were studied in this way¹⁻⁴. Only recently, however, there have appeared in literature first pieces of information about the presence and extent of this conjugative connection in polybenzyltin(IV) compounds⁵ and polyallyltin(IV) compounds⁶ and about the effects of other substituents of the tin atom in the molecules and complexes of benzyl- and allyltin(IV) compounds on the character of the σ - π conjugation.

The present communication deals with application of the ^{13}C and ^{119}Sn NMR spectroscopy to these problems with the aim to confirm (if there exists any) and to try also to determine the relative extent of the σ - π conjugation in series of benzyltin compounds $(\text{C}_6\text{H}_5\text{CH}_2)_{4-n}\text{Sn}(\text{CH}_3)_n$ ($n = 0-3$) (compounds I-IV) and

(C₆H₅CH₂)_{4-n}SnCl_n (*n* = 1–3) (compounds *V*–*VIII*) and in complexes of the latter series mentioned with one or more molecules of coordinating solvent, hexa-deuteriodimethyl sulphoxide, (C₆H₅CH₂)_{4-n}SnCl_n.x(C²H₃)₂SO.

EXPERIMENTAL

The compounds *I*, *III*, *V*, and *VI* were prepared by known methods^{7,8}. Methyltribenzylstannane (*II*) was prepared by the reaction of tribenzylstannyl chloride with methylmagnesium iodide in a yield of 78% according to the procedure given⁷ for preparation of compound *III*. The product forms colourless crystals melting at 68–69°C. For C₂₂H₂₄Sn (407.1) calculated: 64.90% C, 5.94% H, 29.15% Sn; found: 65.06% C, 6.13% H, 28.94% Sn.

Benzyltrichlorostannate was prepared by heating a mixture of tribenzylchlorostannane and tin tetrachloride (1 : 2) to boiling for 3 h. The excess SnCl₄ was exhausted at 50°C by means of a water pump, the product was distilled from the reaction mixture at a pressure of 200 Pa with the use of an oil bath of 120–130°C temperature. The raw product was redistilled in vacuum. The product forms colourless crystals melting at 66–68°C, b.p. 94–96°C/200 Pa. For C₇H₇.Cl₃Sn (316.2) calculated: 26.59% C, 2.23% H, 33.64% Cl, 37.54% Sn; found: 26.87% C, 2.41% H, 33.59% Cl, 37.26% Sn.

The ¹³C and ¹¹⁹Sn NMR spectra were measured with a JNM-FX 100 apparatus (JEOL, Japan) at 25.047 and 37.14 MHz, respectively. Measured were c. 20% or saturated solutions (in the case of less soluble substances) in deuteriochloroform and hexadeuteriodimethyl sulphoxide. The measurement conditions are given in detail elsewhere^{9,10}. The ¹³C chemical shifts were related to a suitable solvent signal: C²HCl₃ (δ = 77.00), (C²H₃)₂SO (δ = 39.60). The chemical shifts δ(¹¹⁹Sn) were related to external neat tetramethylstannane (δ(¹¹⁹Sn) = 0.0). Positive values denote downfield shifts. If not otherwise stated, all the NMR parameters were measured at 300 K (± 1 K). The ¹³C and ¹¹⁹Sn NMR parameters of compound *IV* were taken from ref.¹.

RESULTS AND DISCUSSION

The σ–π conjugative connection (hyperconjugation) between the Sn–C(1) σ bond and the π electronic system of aromatic ring can occur (as any other type of conjugation) only at suitable mutual geometric arrangement of the two partners. As there exists – in principle – free rotation of the two parts of >Sn–CH₂–C₆H₅ fragment around the C(1)–C(2) connecting line (see Fig. 1), the above-mentioned conjugative connection is substantially affected by the conformation of the molecule, viz. by predominant presence of the conformers having suitable dihedral angles ϑ (Fig. 1). Obviously, the most suitable conditions correspond to the angle value ϑ = 90°, whereas with the Sn–C(1) bond located in the plane of the aromatic ring (ϑ = 0°) no hyperconjugation is possible at all. The extent of hyperconjugation is also affected by the magnitude of Sn–C(1)–C(2) angle (α), which, in ideal case, would also have the value α = 90°, and by the therewith connected proportion of *p* electron character in the Sn–C(1) bond (contributions of the *p* characters of atomic orbitals of the tin and C(1) carbon atoms). A larger extent of the σ–π conjugation can be expected with increasing extent of the *p* electron character of the bond⁶.

Table I summarizes the ^{13}C and ^{119}Sn NMR spectral parameters of the compounds studied. The number of signals and their relative intensities in the NMR spectra of both the isotopes (^{13}C and ^{119}Sn) as well as the $\delta(^{119}\text{Sn})$ and $\delta(^{13}\text{C})$ values fully identify the compounds and confirm high degree of their purity (and so do also the chemical analyses).

The dependence of $\delta(^{119}\text{Sn})$ chemical shifts of the two series of compounds in solutions of a non-coordinating solvent (deuteriochloroform) on the composition of the compounds (see Fig. 2) shows the characteristic U-shaped feature (the $\delta(^{119}\text{Sn})$ value of SnCl_4 was taken from ref.¹¹). The deviations from the (ideally) linear course of the dependence (the connection line of the two extreme points of the dependence) are the greater, the larger are the differences in bond polarities of the central tin atom and the substituents, i.e. the higher are the differences in the distribution of *s* and *p* electron character of the tin-substituent bonds. Therefore, the deviations from linearity are greater for the series $(\text{C}_6\text{H}_5\text{CH}_2)_{4-n}\text{SnCl}_n$ (*I*, *V*–*VII*, and SnCl_4) than for the series $(\text{C}_6\text{H}_5\text{CH}_2)_{4-n}\text{Sn}(\text{CH}_3)_n$ (*I*–*IV* and $(\text{CH}_3)_4\text{Sn}$), and thus also the existence and extent of the σ - π conjugation of the Sn – $\text{C}(1)$ bond and aromatic ring can be expected to be less affected by the substituent CH_3 than by Cl .

The upfield shift (by c. 150 to 460 ppm) in the $\delta(^{119}\text{Sn})$ values of compounds *V*–*VII* connected with the transition from solutions in a non-coordinating solvent (deuteriochloroform) to a coordinating one (hexadeuteriodimethyl sulphoxide) is due to formation of complexes of compounds *V*–*VII* with one or more solvent molecules. The compound *V* is present in the solution in hexadeuteriodimethyl sulphoxide as a trigonally bipyramidal complex $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{SnCl} \cdot (\text{C}^2\text{H}_5)_2\text{SO}$ (ref.⁵), the composition and structure of complexes of compounds *VI* and *VII* is estimated as a pseudooctahedral (trans) complex $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{SnCl}_2 \cdot 2(\text{C}^2\text{H}_5)_2\text{SO}$ and a penta-

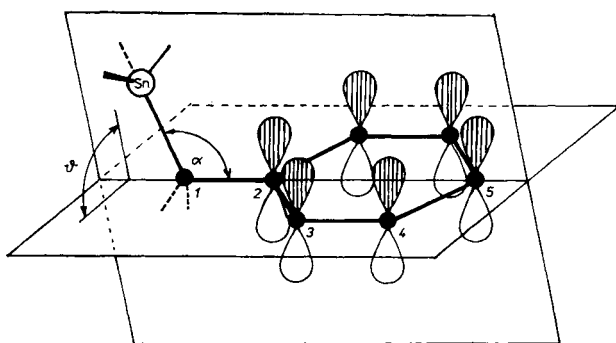


FIG. 1

The geometry of $\text{>Sn-CH}_2\text{-C}_6\text{H}_5$ fragment

TABLE I
The ^{13}C and ^{119}Sn NMR parameters (ppm) of the compounds investigated

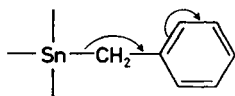
Compound ^a	$\delta(^{13}\text{C})$ ($^nJ(^{119}\text{Sn}, ^{13}\text{C})$, Hz)					$^2J(^{119}\text{Sn}, \text{H})$ Hz
	C(1)	C(2)	C(3)	C(4)	C(5)	
I (C ₆ H ₅ CH ₂) ₄ Sn ^b	18.71 (258.8)	141.38 (37.8)	127.30 (23.6)	128.47 (13.4)	123.49 (15.2)	59.3
II (C ₆ H ₅ CH ₂) ₃ SnCH ₃ ^b	19.10 (271.0)	141.72 (39.1)	127.05 (23.6)	128.32 (13.4)	123.35 (15.0)	60.5 (CH ₂) 50.3 (CH ₃)
III (C ₆ H ₅ CH ₂) ₂ Sn(CH ₃) ₂ ^b	19.64 (283.2)	142.36 (40.3)	126.91 (24.4)	128.32 (13.4)	123.25 (15.0)	62.0 (CH ₂) 52.3 (CH ₃)
IV C ₆ H ₅ CH ₂ Sn(CH ₃) ₃ ^{b,c}	19.95 (290.5)	143.06 — ^d	126.59 (22.6)	128.10 (13.4)	122.86 (14.6)	—10.39 (328.4)
V (C ₆ H ₅ CH ₂) ₃ SnCl ^{b,e}	25.05 (293.0)	137.87 (42.7)	127.69 (31.8)	128.71 (18.0)	124.81 (20.8)	66.1
(C ₆ H ₅ CH ₂) ₃ SnCl ^{e,f}	30.73 (429.6)	140.39 (53.7)	128.11 (34.2)	128.11 (18.3)	124.01 (22.0)	80.9
VI (C ₆ H ₅ CH ₂) ₂ SnCl ₂ ^{b,g}	32.50 (390.6)	134.61 (56.2)	128.32 (46.4)	129.15 (25.7)	126.32 (31.8)	79.6
(C ₆ H ₅ CH ₂) ₂ SnCl ₂ ^{e,f}	49.15 (922.9)	140.09 (90.3)	129.71 (58.6)	127.67 (36.0)	124.60 (42.7)	144.5
VII C ₆ H ₅ CH ₂ SnCl ₃ ^b	38.01 (623.5)	130.27 (106.9)	128.81 (71.5)	129.45 (41.3)	127.87 (50.7)	106.7
C ₆ H ₅ CH ₂ SnCl ₃ ^f	51.98 (1 125.4)	139.96 (123.3)	129.57 (80.6)	128.06 (51.2)	124.94 (62.3)	173.8

^a . ^b In deuteriochloroform. ^c Ref. ¹. ^d Not found. ^e Ref. ⁵. ^f In hexadeuteriodimethyl sulphoxide. ^g 330 K.

gonally bipyramidal complex $C_6H_5CH_2SnCl_3 \cdot 3(C^2H_5)_2SO$, respectively, on the basis of the $\delta(^{119}Sn)$ and $^1J(^{119}Sn, ^{13}C)$ values per analogiam with the corresponding ^{13}C and ^{119}Sn NMR parameters of analogous phenyl-⁹, 1-butyl-^{10,12}, and vinyltin-(IV) compounds¹³. Nevertheless, it is not excluded that the $\delta(^{119}Sn)$ parameter of compounds *VI* and *VII* in hexadeuteriodimethyl sulphoxide also reflects the presence of complex particles of these compounds with lower number of solvent molecules which are with the above-mentioned ones in a rapid equilibrium on the NMR scale¹⁴. In such cases, however, the equilibrium would have to be distinctly shifted in favour of complexes containing higher numbers of solvent molecules.

Relevant values for estimation of the presence and extent of the σ - π conjugation in the compounds of the type studied are those of the coupling constants $^nJ(^{119}Sn, ^{13}C)$ (especially so for $n = 1, 4$, and 5 , in some cases also for $n = 3$) and the $\delta(^{13}C)$ chemical shifts for C(3), C(4), and C(5) carbon atoms.

The Sn—C(1) bond in benzyltin(IV) compounds is, due to the σ - π conjugation represented in Scheme 1, weakened in favour to the C(1)—C(2) bond¹⁵. Conse-



SCHEME 1

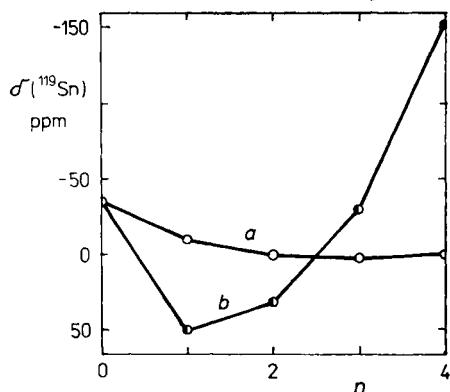


FIG. 2

The dependence of $\delta(^{119}Sn)$ chemical shifts of the compounds $(C_6H_5CH_2)_{4-n}Sn(CH_3)_n$ (*a*) and $(C_6H_5CH_2)_{4-n}SnCl_n$ (*b*) on the composition (the n parameter) in a non-coordinating solvent (deuteriochloroform)

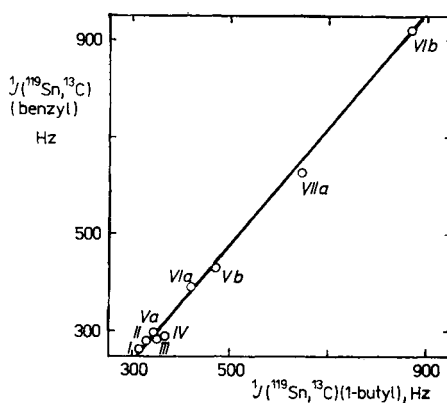


FIG. 3

The interdependence of $^1J(^{119}Sn, ^{13}C)$ values of benzyl- and 1-butyltin(IV) compounds (*a* deuteriochloroform, *b* hexadeuteriodimethyl sulphoxide)

quently, the values of the coupling constants ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C}(1))$ of benzyltin(IV) compounds are generally lower than the ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C})$ values of alkyltin(IV) compounds. Hence, the values of differences between the coupling constants ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C}(1))$ of benzyl- and alkyltin(IV) (e.g. 1-butyltin(IV)) compounds can be considered (provided the shapes of coordination polyhedrons of the two series of compounds are identical or little different) to be a relative measure of the σ - π conjugative connection in different types of benzyltin(IV) compounds⁵.

Figure 3 presents the mutual dependence between the ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C}(1))$ values of the benzyltin(IV) compounds *I*–*VII* and the ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C})$ values of analogous 1-butyltin(IV) compounds^{10,12,16,17}. The dependence in Fig. 3 is strictly linear: the ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C})$ values increase in both types of organotin(IV) compounds with increasing number of the electronegative substituents Cl and with increasing coordination number of the central tin atom. Hence, the shapes of the coordination polyhedrons are almost identical or at least very close. The analytical form of the dependence:

$${}^1J({}^{119}\text{Sn}, {}^{13}\text{C}(1))(\text{benzyl}) = (1.19 \pm 0.03) {}^1J({}^{119}\text{Sn}, {}^{13}\text{C})(1\text{-butyl}) - (123.6 \pm 14.07); \quad r = 0.998, \quad N = 9 \quad (1)$$

(r is the regression coefficient, N number of points) further shows (particularly the slope value, which is greater than 1) that with increasing number of electronegative substituents and of the coordination number of central tin atom, the ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C}(1))$ values of benzyltin(IV) compounds increase more steeply than the ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C})$ values of analogous 1-butyltin(IV) compounds do, thus the ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C})$ values are identical for the two types of organotin compounds in the region about 625 Hz. In the benzyltin(IV) compounds having still higher ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C}(1))$ value the σ - π conjugation is no more likely.

The differences Δ^1J defined as ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C})(1\text{-butyl}) - {}^1J({}^{119}\text{Sn}, {}^{13}\text{C}(1))(\text{benzyl})$ are given in Table II. It can be seen that the Δ^1J value increases, in the compound series *I*–*IV*, with increasing number of methyl groups in the molecules $(\text{C}_6\text{H}_5\text{CH}_2)_{4-n}\text{Sn}(\text{CH}_3)_n$ and, on the other hand, it decreases in the compounds *IV*–*VII* with increasing number of the electronegative substituents Cl. Further decrease can be observed in connection with formation of the complexes of compounds *V* and *VI* with one and two molecules, resp., of a coordinating solvent. With the compound *VI* in hexadeuteriodimethyl sulphoxide, the difference Δ^1J even has negative sign. Generally higher values ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C}(1))$ of benzyltin(IV) compounds as compared with the ${}^1J({}^{119}\text{Sn}, {}^{13}\text{C})$ of analogous 1-butyltin(IV) compounds, and hence also $\Delta^1J < 0$, can be expected (with regard to the presence of a phenyl nucleus at β position to the tin atom) in such cases where no σ - π conjugative connection takes place¹⁵. The decrease in the extent of σ - π conjugative connection with decreasing number of methyl groups in the series

$(\text{C}_6\text{H}_5\text{CH}_2)_{4-n}\text{Sn}(\text{CH}_3)_n$ and with increasing number of chlorine atoms in the series $(\text{C}_6\text{H}_5\text{CH}_2)_{4-n}\text{SnCl}_n$ is consistent with the idea of decreasing share of the p electron of the Sn—C(1) bond which, according to the Bent rule¹⁸, is concentrated in bonds to more electronegative substituents. The generally lower extent of σ - π conjugation in the complexes of compounds *V* and *VI* with hexadeuteriodimethyl sulphoxide, as compared with the simple pseudotetrahedral compounds *V* and *VI* (solutions in deuteriochloroform), is caused by a further decrease in the p electron character of the Sn—C(1) bond due to a change in the structure of the coordination polyhedra and the therewith connected change in the hybridization type of the tin atoms participating in this bond (the rehybridization $sp^3 \rightarrow sp^2$ and $sp^2 \rightarrow sp$, respectively)^{5,8-10,12,13}.

Significant features of the presence of σ - π conjugation in benzyltin(IV) compounds and (first of all) of favourable geometry conditions for its formation are the non-zero and relatively high values of the ${}^5J(^{119}\text{Sn}, {}^{13}\text{C})$ coupling constants and, further, the fact that the ${}^5J(^{119}\text{Sn}, {}^{13}\text{C})$ values are greater than ${}^4J(^{119}\text{Sn}, {}^{13}\text{C})$ values¹ for all the compounds studied. For the tetraorganotin(IV) compounds having at least one $\text{C}_6\text{H}_5\text{CH}_2$ substituent, i.e. for the compound series *I*–*IV*, it is possible, according to ref.¹ on the basis of the values ${}^5J(^{119}\text{Sn}, {}^{13}\text{C}) \sim 15$ Hz, to assign the magnitude

TABLE II
The Δ^1J , ${}^{13}\text{C}$ SCS, and σ_{R}^0 values for compounds *I*–*VII*

Compound ^a	Δ^1J^b , Hz	${}^{13}\text{C}$ SCS ^{c,d}					σ_{R}^0e
		C(1)	C(2)	C(3)	C(4)	C(5)	
<i>I</i> ^f	54.8	-2.68	+3.61	-1.70	+0.30	-1.81	-0.21
<i>II</i> ^f	59.3	-2.29	+3.95	-1.95	+0.15	-1.95	-0.22
<i>III</i> ^f	65.5	-1.75	+4.59	-2.09	+0.15	-2.05	-0.23
<i>IV</i> ^f	77.7	-1.44	+5.29	-2.41	-0.07	-2.44	-0.24
<i>V</i> ^f	46.5	+3.66	+0.10	-1.31	+0.54	-0.49	—
<i>VI</i> ^f	29.3	+11.11	-3.16	-0.68	+0.98	+1.02	—
<i>VII</i> ^f	21.5	—	-7.50	-0.19	+1.28	+2.57	—
<i>V</i> ^g	34.8	+9.34	+2.62	-0.89	-0.06	-1.29	—
<i>VI</i> ^{g,h}	-51.8	+27.76	+2.32	+0.71	-0.50	-0.70	—
<i>VII</i> ^g	—	+30.59	+2.19	+0.57	-0.11	-0.36	—

^a See Table I. ^b ${}^1J(^{119}\text{Sn}, {}^{13}\text{C})$ (1-butyl) — ${}^1J(^{119}\text{Sn}, {}^{13}\text{C}(1))$ (benzyl), see the text. ^c $\delta(^{13}\text{C})$ (compounds *I*–*VII*) — $\delta(^{13}\text{C})$ (toluene), see the text. ^d $\delta(^{13}\text{C})$ (toluene): 21.39 (C1), 137.77 (C2), 129.00 (C3), 128.17 (C4), 125.30 (C5). ^e For the substituents $(\text{C}_6\text{H}_5\text{CH}_2)_{3-n}(\text{CH}_3)_n \cdot \text{SnCH}_2$ — ($n = 0-3$). ^f In deuteriochloroform. ^g In hexadeuteriodimethyl sulphoxide. ^h Di-1-butylstannyl dichloride in hexadeuteriodimethyl sulphoxide has ${}^1J(^{119}\text{Sn}, {}^{13}\text{C}) = 871.1$ Hz.

of about 60° to the dihedral angle Θ . The same conclusions follow from the calculations of dihedral angles from the $^3J(^{119}\text{Sn}, ^{13}\text{C})$ values of compounds *I–IV* by means of an equation of Karplus type which was derived by Doddrell et al.¹⁹ for tetrahedral organometallic compounds with benzyl (and similar) substituents. The values $^3J(^{119}\text{Sn}, ^{13}\text{C})$ and $^5J(^{119}\text{Sn}, ^{13}\text{C})$ of compounds *V–VII* cannot be used for the calculation of dihedral angles, because they are very much affected by the presence of electronegative Cl substituents and – their complexes with hexadeuteriodimethyl sulphoxide, in addition to it – by a changed coordination situation about the central tin atom. It is difficult to estimate the extent of this influence. Nevertheless, even for these compounds it can be concluded, both from the high $^5J(^{119}\text{Sn}, ^{13}\text{C})$ and $^3J(^{119}\text{Sn}, ^{13}\text{C})$ value and especially from the fact that $^5J(^{119}\text{Sn}, ^{13}\text{C}) > ^4J(^{119}\text{Sn}, ^{13}\text{C})$, that the magnitude of dihedral angles Θ is favourable for the σ - π conjugation. For two tribenzyltin(IV) compounds with a polar substituent and, in addition to it, differing from each other in the coordination at the central tin atom, viz. for the pseudotetrahedral compound $[(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}]_2\text{O}$ and the trigonally bipyramidal polymer $\{(\text{C}_6\text{H}_5\text{CH}_2)_3\text{SnOCOCH}_3\}_n$, we used the published diffraction data^{20,21} to calculate the Θ dihedral angles in crystal state of the compounds mentioned: 78° and 85° , respectively, i.e. values approaching the ideal cases.

A direct consequence of the σ - π conjugation in the $\text{>Sn-CH}_2\text{-C}_6\text{H}_5$ grouping consists in distinct donor abilities of the >Sn-CH_2 group to the resonance positions of aromatic system. The extent of the σ - π conjugation can then be reflected by the values of substitution chemical shifts (^{13}C SCS), i.e. the differences between the chemical shifts $\delta(^{13}\text{C})$ of carbon atoms of the benzyl substituent and those of the reference compound (i.e. toluene). The ^{13}C SCS values thus defined are summarized for the compounds studied in Table II. From the table it can be seen that with compounds *I–IV* the ^{13}C SCS values of C(3) and C(5) carbon atoms (i.e. the carbon atoms at *o*- and *p*-positions of the phenyl ring with respect to the $\text{R}'_3\text{SnCH}_2$ substituents (which denote the whole rest of the molecule or complex of the benzyltin(IV) compound except one phenyl group) show a distinct upfield shift, whereas those of C(4) atom (*m*-position) show a relatively small downfield shift. Hence, replacement of hydrogen atom in toluene methyl group by an $\text{R}'_3\text{Sn}$ group brings about a marked increase of π electron density (π electron charge)²² in the vicinity of C(3) and C(5) atoms. Thus the substituents $(\text{C}_6\text{H}_5\text{CH}_2)_{3-n}(\text{CH}_3)_n\text{SnCH}_2\text{—}$ can be considered to be relatively pure resonance donors with regard to the ^{13}C SCS values of C(3) and C(5) carbon atoms in compounds *I–IV*, and it is possible to calculate their σ_{R}^0 constants on the basis of ref.²³. These constants are also given in Table II. It is noteworthy that the resonance donor ability of the substituents $(\text{C}_6\text{H}_5\text{CH}_2)_{3-n}(\text{CH}_3)_n\text{SnCH}_2\text{—}$ increases with increasing number of methyl groups (*n*) in accordance with the above conclusions (see the discussion of the $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constants). The donor properties of the substituents $(\text{C}_6\text{H}_5\text{CH}_2)_{3-n}\text{Cl}_n\text{SnCH}_2\text{—}$ in compounds *V–VII* ($n = 1–3$, deuteriochloroform)

are substantially weaker than those of the substituents derived from compounds *I–IV*, which is in accordance with the prediction made in the paragraph on $\delta(^{119}\text{Sn})$ and the conclusions made from the analysis of $^1J(^{119}\text{Sn}, ^{13}\text{C})$ values. With increasing number of chlorine atoms the donor abilities further decrease, and, on the other hand, the acceptor ability increases, due probably to the contribution of inductive effects of these electronegative atoms. This is indicated by further upfield shifts in $\delta(^{13}\text{C})$ of C(3) and C(5) carbon atoms (increasing ^{13}C SCS values) and by diminishing differences in the ^{13}C SCS between the C(4) and C(5) carbon atoms. With the compounds *VI* and *VII* the ^{13}C SCS values of these carbon atoms even have positive sign. By formation of the donor–acceptor bond between the central tin atom and the donor oxygen atom in the $(\text{C}^2\text{H}_3)_2\text{SO}$ ligand (complexes of compounds *V–VII* in hexadeuteriodimethyl sulphoxide solutions) substantially increases the electron density at the tin atom and, consequently, also the donor abilities of the $(\text{C}_6\text{H}_5\text{CH}_2)_{3-n}(\text{Cl})_n[(\text{C}^2\text{H}_3)_2\text{SO}]_x\text{SnCH}_2-$ substituents as compared with the corresponding substituents $(\text{C}_6\text{H}_5\text{CH}_2)_{3-n}(\text{Cl})_n\text{SnCH}_2-$. The fact that the changes in ^{13}C SCS of C(4) and C(5) carbon atoms are mutually comparable for the two types of substituents in the simple compounds *V–VII* and its complexes rather indicates an inductive effect. The share of σ - π conjugation in the overall donor effect of the complex substituents in compounds *V–VII* is very small.

The analysis of $\delta(^{119}\text{Sn})$ chemical shifts, $^1J(^{119}\text{Sn}, ^{13}\text{C})$ coupling constants ($n = 1, 3, 4,$ and 5), and $\delta(^{13}\text{C})$ chemical shifts of the C(3), C(4), and C(5) carbon atoms has provided mutually consistent results which indicate that the geometry conditions necessary for formation of a σ - π conjugative connection between the polarized Sn–C(1) σ bond and π electron system of phenyl group are fulfilled in all the studied compounds *I–VII* as well as in their complexes *V–VII* with one or more molecules of the coordinating solvent (hexadeuteriodimethyl sulphoxide). The extent of this connection slightly decreases with decreasing number of methyl groups in compounds *I–IV* and dramatically decreases with increasing replacement of organic groups by the polar substituents Cl in compounds *V–VII* and in complexes of these compounds with one or more molecules of a coordinating solvent.

REFERENCES

1. Kitching W., Drew G., Adcock W., Abeywickrema A. N.: *J. Org. Chem.* **46**, 2252 (1981) and the literature quoted therein.
2. Kitching W., Olszowy H. A., Schott I., Adcock W., Cox D. P.: *J. Organomet. Chem.* **310**, 269 (1986).
3. Adcock W., Gaugodawila H., Kok G. B., Iyer V. S., Kitching W., Drew G. M., Young D.: *Organometallics* **6**, 156 (1987).
4. Matarosso-Tchiroukhine E., Cadiot P.: *Can. J. Chem.* **61**, 2476 (1983).
5. Lyčka A., Jirman J., Koloničný A., Holeček J.: *J. Organomet. Chem.* **333**, 305 (1987).
6. Cauletti C., Furlani C., Grandinetti F., Marton D.: *J. Organomet. Chem.* **315**, 287 (1986).
7. Cattanach C. J., Mooney E. F.: *Spectrochim. Acta*, **A 24**, 407 (1968).

8. Verdonck L., Van der Kelen G. P.: *J. Organomet. Chem.* 5, 532 (1966).
9. Holeček J., Nádvorník M., Handlíř K., Lyčka A.: *J. Organomet. Chem.* 241, 177 (1983).
10. Nádvorník M., Holeček J., Handlíř K., Lyčka A.: *J. Organomet. Chem.* 275, 43 (1984).
11. Burke J. J., Lauterbur P. C.: *J. Am. Chem. Soc.* 83, 326 (1961).
12. Holeček J., Nádvorník M., Handlíř K., Lyčka A.: *J. Organomet. Chem.* 315, 299 (1986).
13. Holeček J., Handlíř K., Nádvorník M., Teleb S. M. T., Lyčka A.: *J. Organomet. Chem.* 339, 61 (1988).
14. Holeček J., Handlíř K., Černý V., Nádvorník M., Lyčka A.: *Polyhedron* 6, 1037 (1987).
15. Fedorov L. A.: *Zh. Strukt. Khim.* 25, 35 (1984).
16. Steinborn D., Taube R., Radeaglia R.: *J. Organomet. Chem.* 229, 159 (1982).
17. Mitchell T. J.: *J. Organomet. Chem.* 59, 189 (1973).
18. Bent H. A.: *Chem. Rev.* 61, 275 (1961).
19. Doddrell D., Burfitt I., Kitching W., Bullpitt M., Lee C., Mynott R. J., Considine J. L., Kuivila H. G., Sarma R. H.: *J. Am. Chem. Soc.* 96, 1640 (1974).
20. Glidewell C., Liles D. C.: *Acta Crystallogr.*, B 35, 1689 (1979).
21. Alcock N. W., Timms R. E.: *J. Chem. Soc.*, A 1873 (1968).
22. Vanermen G., Toppet S., Van Beylen M., Geerling P.: *J. Chem. Soc.*, Perkin Trans. 2, 1986, 699.
23. Adcock W., Cox D. P., Kitching W.: *J. Organomet. Chem.* 133, 393 (1977).

Translated by J. Panchartek.