^{13}C AND ^{119}Sn NMR SPECTRA OF SOME TRIPHENYLTIN 4-SUBSTITUTED BENZOATES DISSOLVED IN COORDINATING AND NON-COORDINATING SOLVENTS

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

[a] *Research Institute of Organic Syntheses, 532 18 Pardubice - Rybitví, and*
[b] *Department of General and Inorganic Chemistry, Institute of Chemical Technology, 532 10 Pardubice*

Received February 13th, 1984

^{13}C and ^{119}Sn NMR spectra of the title compounds $(C_6H_5)_3SnOC(O)C_6H_4$-4-X, where X = H, NH_2, OCH_3, $C(CH_3)_3$, CH_3, $NHCOCH_3$, Cl, and NO_2, have been studied in coordinating (pentadeuteriopyridine, hexadeuteriodimethyl sulphoxide) and non-coordinating solvents (deuteriochloroform). From the NMR spectral parameters it follows that all the compounds studied, dissolved in the coordinating solvents, form donor–acceptor complexes with one solvent molecule. Discussed are the differences in composition and structure of the compounds in the two types of solvents as well as influence of substituents on values of the parameters of the ^{13}C and ^{119}Sn NMR spectra.

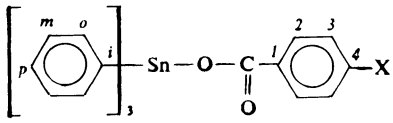
Solutions of triorganyltin carboxylates in non-coordinating solvents contain monomeric particles of the compounds, irrespective of their structural arrangement in solid phase. This fact was proved in the previous communication[1] for a large group of triphenyltin(IV) carboxylates (of both aliphatic and aromatic carboxylic acids) by means of a ^{13}C and ^{119}Sn NMR spectral method developed earlier in our laboratory[2]. The tetracoordinated tin atom of the molecules of triorganyltin(IV) carboxylates represents a coordinatively unsaturated system which can form a donor–acceptor complex in the presence of a donor of electron pair (*e.g.* a coordinating solvent molecule). The present communication deals with a study of ^{13}C and ^{119}Sn NMR spectra of solutions of a selected group of triphenyltin(IV) 4-substituted benzoates $(C_6H_5)_3SnOC(O)C_6H_4$-4-X, where X = H, NH_2, OCH_3, $C(CH_3)_3$, CH_3, $NHCOCH_3$ Cl, and NO_2 in coordinating (pentadeuteriopyridine, hexadeuteriodimethyl sulphoxide) and non-coordinating (deuteriochloroform) solvents by means of ^{13}C and ^{119}Sn NMR spectral method. The aim of this study is to confirm the existence of the donor–acceptor complexes, to determine their composition and probable structure and, furthermore, to verify the nature and extent of effects of solvent type and character of the substituent in the phenyl ring of the benzoate group on the values of the ^{13}C and ^{119}Sn NMR spectral parameters.

EXPERIMENTAL

All the studied 4-substituted triphenyltin(IV) benzoates were prepared according to described procedure[1]. The ^{13}C and ^{119}Sn NMR spectra of the compounds were measured in solutions of deuteriochloroform, pentadeuteriopyridine, and hexadeuteriodimethyl sulphoxide at approximate (w/v) concentrations of 4% (^{119}Sn NMR) and 20% or saturated solutions (^{119}Sn, ^{13}C NMR) with a JNM-FX 100 apparatus (JEOL, Japan) at 25·047 MHz (^{13}C, int. $(CH_3)_4Si$) or 37·14 MHz (^{119}Sn, ext. neat $(CH_3)_4Sn$) at 300 K. Positive values of the chemical shifts denote the downfield shifts. The NMR spectra were identified and interpreted as in refs[1-3].

RESULTS

The chemical shifts $\delta(^{119}Sn)$ and coupling constants $^nJ(^{119}Sn\ ^{13}C)$ of the ca. 20% or saturated solutions of the compounds studied in deuteriochloroform, pentadeuteriopyridine, and hexadeuteriodimethyl sulphoxide are given in Table I. The $\delta(^{119}Sn)$ chemical shifts of the *c.* 4% solutions were shifted upfields by at most 1 ppm. Table II gives the $\delta(^{13}C)$ chemical shifts of the individual carbon atoms arranged in the same order of solvents. Their denotation follows from formula *I*. From the two Tables it



I

is seen that practically all parameters of the ^{13}C and ^{119}Sn NMR spectra depend, more or less, on both the type of solvent and the character of the X substituent. Generally it can be stated that the solvent effect is more distinct on the parameters characterizing the triphenylstannyl group, whereas the X substituent effect makes itself felt in the benzoate residue to a greater extent, although it cannot be neglected in the remaining parts of the molecule.

Effect of the Type of Solvent

The solvent nature affects most markedly the NMR spectral parameters which characterize the central tin atom and its immediate surroundings, *i.e.* the three $C_{(i)}$ atoms and their links to the central atom in the grouping $(C_6H_5)_3Sn$. This effect gradually decreases with increasing distance from the tin atom. This fact alone indicates donor–acceptor interaction between the tin atom and the corresponding donor atoms of pentadeuteriopyridine and hexadeuteriodimethyl sulphoxide.

The $\delta(^{119}Sn)$, $\delta(^{13}C)_{(i)}$, and $^1J(^{119}Sn^{13}C)$ parameters of the compounds studied in deuteriochloroform are significant for quasitetrahedral arrangement of the $(C_6H_5)_3$. .SnO grouping and, hence, for monomeric character of their molecules[1,2]. The same

parameters measured in the coordinating solvents indicate *trans*-trigonally bipyramidal geometry of the environment of the tin atom in the donor–acceptor complexes[2]. A good linear correlation (*1*) was found between the $^1J(^{119}Sn^{13}C)$ and $\delta(^{119}Sn)$ values.

$$^1J(^{119}Sn^{13}C) = \alpha \,.\, \delta(^{119}Sn) + \beta \qquad (1)$$

Parameters of the linear correlations are given in Table III.

The $\delta(^{13}C)$ chemical shifts of carbon atoms of the $(C_6H_5)_3Sn$ group, except for $\delta(^{13}C)_{(i)}$, are relatively little sensitive to the change in solvent nature. It is noteworthy, however, that values of the differences $\delta(^{13}C)_{(p)} - \delta(^{13}C)_{(m)}$, which characterize the overall π electron density of the phenyl ring[4], are by about one half smaller for the compounds measured in the coordinating solvents (0·53 – 0·68 ppm) than the values determined in deuteriochloroform (1·20 – 1·60 ppm.)

Also observable is the effect of solvent character on the chemical shifts $\delta(^{13}C)$ of some carbon atoms of the benzoate group. The coordination change at the tin atom causes an upfield shift of $\delta(^{13}C)_{(COO)}$ by 0·6 – 3·5 ppm and a downfield shift of $\delta(^{13}C)_{(1)}$ by 1·7 – 4·8 ppm. The $\delta(^{13}C)_{(4)}$ shifts in the coordinating solvents differ by −5·3 to +2·4 ppm from the same values in the non-coordinating solvents. Changes in the $\delta(^{13}C)_{(2)}$ and $\delta(^{13}C)_{(3)}$ chemical shifts (or also that of the carbon atom of substituent X, $\delta(^{13}C)_{(x)}$ are negligibly small and vary within the experimental error.

TABLE I
$\delta(^{119}Sn)$ and $^1J(^{119}Sn^{13}C)$ values of triphenylstannyl 4-substituted benzoates

Substituent X	$\delta(^{119}Sn)$, ppm			$^1J(^{119}Sn^{13}C)$, Hz[b]		
	C^2HCl_3[a]	$C_5{}^2H_5N$	$(C^2H_3)_2SO$	C^2HCl_3[a]	$C_5{}^2H_5N$	$(C^2H_3)_2SO$
H	−109·9	−241·8	−261·0	648·4	805·7	834·0
NH_2	−120·9	−213·9	−254·0	650·4	761·7	822·2
OCH_3	−115·0	−233·8	−259·3	649·4	793·5	830·1
$C(CH_3)_3$	−112·4	−240·3	−260·2	648·2	800·8	832·6
CH_3	−112·6	−237·2	−259·8	649·4	800·8	832·6
$NHCOCH_3$	−110·2	−237·4	−259·6	649·4	798·4	831·3
Cl	−104·9	−245·7	−261·6	647·5	808·2	835·0
NO_2	− 96·1	−252·3	−263·2	646·5	820·4	837·9

[a] The values taken from ref.[1]; [b] the $^nJ(^{119}Sn^{13}C)$ values are almost identical for $n = 2$, 3, and 4, being: $^2J = 49{\cdot}0 \pm 0{\cdot}3$ (for the solution in C^2HCl_3), $44{\cdot}0 \pm 1{\cdot}0$ ($C_5{}^2H_5N$), $46{\cdot}0 \pm 1{\cdot}0$ ($(C^2H_3)_2$.SO), and similarly $^3J = 64{\cdot}2 \pm 0{\cdot}3$, $69{\cdot}0 \pm 1{\cdot}5$, $70{\cdot}4 \pm 1{\cdot}0$ Hz, $^4J = 13{\cdot}5 \pm 0{\cdot}2$, $14{\cdot}0 \pm 1{\cdot}0$, $14{\cdot}6 \pm 1{\cdot}0$ Hz.

TABLE II

The $\delta(^{13}C)$ values of triphenyltin(IV) 4-substituted benzoates

$\delta(^{13}C)$ ppm[a,b]	Substituent X							
	H	NH_2	OCH_3	$C(CH_3)_3$	CH_3	$NHCOCH_3$	Cl	NO_2
$C_{(i)}$	138·24	138·79	138·52	138·41	138·41	138·41	138·06	137·47
	142·69	142·49	142·64	142·74	142·59	142·64	142·59	142·49
	143·35	143·58	143·47	143·36	143·36	143·46	143·21	143·00
$C_{(o)}$	136·80	136·80	136·81	136·85	136·85	136·85	136·81	136·77
	137·42	137·47	137·47	137·42	137·42	137·42	137·37	137·47
	136·37	136·45	136·37	136·34	136·39	136·44	136·39	136·25
$C_{(m)}$	128·81	128·73	128·78	128·81	128·81	128·90	128·89	128·97
	129·04	129·04	129·04	128·99	128·99	129·09	129·09	129·19
	128·38	128·30	128·30	128·35	128·40	128·45	128·45	128·49
$C_{(p)}$	130·06	129·87	129·99	130·03	130·03	130·12	130·14	130·37
	129·67	129·12	129·67	129·63	129·67	129·72	129·72	129·58
	128·96	128·84	128·88	128·89	128·98	130·49	129·08	129·02
$C_{(COO)}$	172·79	173·02	172·56	172·82	172·88	172·38	171·59	170·10
	171·00	172·42	171·00	171·10	171·15	171·05	169·84	168·57
	169·39	170·25	169·16	169·29	169·34	168·90	168·41	167·40
$C_{(1)}$	130·37	119·18	122·69	128·27	[c]	125·93	129·09	136·42
	134·65	121·29	127·09	[c]	132·11	[c]	133·91	141·08
	134·26	120·89	126·90	131·76	131·52	128·45	133·52	140·54
$C_{(2)}$	130·53	132·63	132·64	130·51	130·61	131·88	131·93	131·43
	130·50	132·89	132·45	130·41	130·60	131·62	132·01	131·19
	129·39	131·30	131·26	129·28	129·52	130·49	131·27	130·56
$C_{(3)}$	128·07	113·49	113·30	125·10	128·80	118·67	128·35	123·16
	128·36	113·59	113·64	125·24	128·99	118·90	128·41	123·49
	128·40	112·59	113·33	124·89	128·74	118·21	128·30	123·42
$C_{(4)}$	132·59	150·84	163·66	156·25	143·18	142·06	138·91	150·12
	131·87	153·21	162·82	150·97	141·90	143·71	137·37	149·90
	131·53	152·04	161·83	154·18	141·36	142·43	[c]	149·23
$C_{(x)}$	—	—	55·17	34·99[d]	21·54	168·53[e]	—	—
			55·30	31·15[d]	20·33	169·20[e]		
			55·35	34·63[d]	21·18	168·90[e]		

[a] The chemical shift values $\delta(^{13}C)$ of the individual carbon atoms are given in the solvents order: C^2HCl_3, $C_5{}^2H_5N$, $(C^2H_3)_2SO$; [b] the values for C^2HCl_3 are taken from ref.[1]; [c] overlap; [d] for the carbon atoms of methyl groups 31·29, 30·55, 31·07; [e] for the carbon atom of the methyl group 24·56, 24·36, 24·30.

The parameters of ^{119}Sn NMR spectra give significant information on dynamic properties of formation of complexes. The derivative with the 4-$NHCOCH_3$ substituent dissolved in hexadeuteriodimethyl sulphoxide was diluted 1 : 1 with deuteriochloroform (v/v), and the measured chemical shift was $\delta(^{119}Sn)$ −248·4 ppm. The same derivative was dissolved in a 1 : 4 (v/v) mixture of hexadeuteriodimethyl sulphoxide and deuteriochloroform, and the $\delta(^{119}Sn)$ chemical shift measured was −218·0 ppm. The measurements were repeated after 24 h, and the $\delta(^{119}Sn)$ values found were, within experimental error, the same as those measured immediately after preparation of the solutions. These results show that the formation of complexes of triphenyltin(IV) benzoates with coordinating solvents represents a reversible reaction whose equilibrium is rapidly established. The difference in the $\delta(^{119}Sn)$ chemical shifts obtained in 4 and 20% solutions of the triphenyltin(IV) benzoates did not exceed 1 ppm (see above), which means that the equilibrium is shifted in favour of formation of the complex compounds.

Effect of Character of the X *Substituent*

The $\delta(^{13}C)$ chemical shifts of the carbon atoms of the benzoate group vary within relatively broad limits, they are, however, not distinctly different from analogous values of purely organic 4-substituted benzoates[5]. It is possible to apply to them the concept of additivity of contributions of substituent chemical shifts (SCS) (ref.[6,7]) in all the solvents used within accuracy of this concept. Greater deviations were only observed with the derivatives having X = NH_2 and $NHCOCH_3$.

The X substituent effects on the $\delta(^{119}Sn)$, $^1J(^{119}Sn^{13}C)$, $\delta(^{13}C)_{(COO)}$, and $\delta(^{13}C)_{(1)}$ parameters can be described satisfactorily by the Hammett correlations of the type

$$\Delta P = \varrho\sigma_p + \varrho_0 , \qquad (2)$$

TABLE III

The parameters of linear correlation according to Eq. (*1*)

Solvent	α, Hz ppm^{-1}	β, Hz	N[a]	r[b]
C^2HCl_3	−0·16 ± 0·03	631·13 ± 2·84	8	0·930
$C_5{}^2H_5N$	−1·50 ± 0·06	441·19 ± 14·73	8	0·995
$(C^2H_3)_2SO$	−1·71 ± 0·07	387·66 ± 18·33	8	0·995
[c]	−1·51 ± 0·02	439·26 ± 6·06	16	0·998

[a] Number of pairs; [b] the regression coefficient; [c] the data from the two coordinating solvents.

where P means the corresponding parameters and ΔP means the difference of the parameters between the substituted and non-substituted triphenyltin(IV) benzoates. Table IV gives the values of the correlation constants. The values for $X = NH_2$ only deviate from the satisfactory linear dependences. The $\delta(^{119}Sn)$ shifts in deuteriochloroform show positive dependence on σ_p, whereas in the coordinating solvents the coefficient is $\varrho < 0$. The correlation coefficients ϱ of the dependences $^1J(^{119}Sn^{13}C)$ *vs* σ_p have opposite signs in the both solvent types as compared with the respective dependences $\delta(^{119}Sn)$ *vs* σ_p. In accordance with refs[7,8], the $\delta(^{13}C)_{(COO)}$ chemical shifts show negative values of the ϱ correlation coefficients in the both solvents types, whereas, on the contrary, the dependence $\delta(^{13}C)_{(1)}$ *vs* σ_p has positive slopes in all the cases. Small upfield and downfield shifts of $\delta(^{13}C)_{(COO)}$ and $\delta(^{13}C)_{(1)}$, respectively, of the coordinated 4-substituted triphenyltin(IV) benzoates as compared with the same values of the non-coordinated molecules are connected with increased donor ability of the coordinated group $(C_6H_5)_3SnO$ as compared with the same non-coordinated group[7,9].

Effects of the X substituents on the $\delta(^{13}C)$ chemical shifts of the carbon atoms of triphenylstannyl group and on the values of $^nJ(^{119}Sn^{13}C)$ (n = 2, 3, and 4)

TABLE IV

The parameters of linear correlation according to Eq. (*2*)

P	Solvent	ϱ	ϱ_0	N[a]	r[b]
$\delta(^{119}Sn)$	C^2HCl_3	17·98 ± 0·61[c]	0·00 ± 0·23[c]	8	0·997
$\delta(^{119}Sn)$	$C_5{}^2H_5N$	−24·26 ± 5·43[c]	3·39 ± 2·07[c]	8	0·877
$\delta(^{119}Sn)$	$C_5{}^2H_5N$	−16·08 ± 2·18[c]	1·44 ± 0·75[c]	7[e]	0·957
$\delta(^{119}Sn)$	$(C^2H_3)_2SO$	− 5·69 ± 1·37[c]	1·02 ± 0·52[c]	8	0·861
$\delta(^{119}Sn)$	$(C^2H_3)_2SO$	− 3·60 ± 0·46[c]	0·52 ± 0·15[c]	7[e]	0·962
$^1J(^{119}Sn^{13}C)$	C^2HCl_3	− 2·87 ± 0·46[d]	1·78 ± 0·18[d]	8	0·930
$^1J(^{119}Sn^{13}C)$	$C_5{}^2H_5N$	36·10 ± 8·60[d]	−6·10 ± 3·27[d]	8	0·864
$^1J(^{119}Sn^{13}C)$	$C_5{}^2H_5N$	22·85 ± 2·56[d]	−2·94 ± 0·88[d]	7[e]	0·970
$^1J(^{119}Sn^{13}C)$	$(C^2H_3)_2SO$	9·92 ± 2·26[d]	−1·79 ± 0·86[d]	8	0·874
$^1J(^{119}Sn^{13}C)$	$(C^2H_3)_2SO$	6·59 ± 1·05[d]	−0·99 ± 0·36[d]	7[e]	0·942
$\delta(^{13}C)_{(COO)}$	C^2HCl_3	− 2·25 ± 0·37[c]	−0·58 ± 0·14[c]	8	0·928
$\delta(^{13}C)_{(COO)}$	$C_5{}^2H_5N$	− 2·71 ± 0·09[c]	−0·30 ± 0·09[c]	8	0·975
$\delta(^{13}C)_{(COO)}$	$(C^2H_3)_2SO$	− 1·96 ± 0·24[c]	−0·42 ± 0·09[c]	8	0·956
$\delta(^{13}C)_{(1)}$	C^2HCl_3	12·03 ± 1·93[c]	−2·85 ± 0·78[c]	7	0·941
$\delta(^{13}C)_{(1)}$	$C_5{}^2H_5N$	13·53 ± 2·35[c]	−3·05 ± 1·02[c]	6	0·944
$\delta(^{13}C)_{(1)}$	$(C^2H_3)_2SO$	13·21 ± 2·19[c]	−2·95 ± 0·83[c]	8	0·927

[a] Number of pairs; [b] the regression coefficient; [c] ppm; [d] Hz; [e] without $X = NH_2$.

coupling constants are slight and usually do not exceed the limits of experimental error.

DISCUSSION

Whereas in deuteriochloroform solution all the studied 4-substituted triphenyltin(IV) benzoates are present as simple molecules with the tin atom in tetrahedral coordination, the presence of coordinating solvents will cause formation of donor–acceptor complexes between the solute and solvent. Values of the characteristic parameters of the ^{13}C and ^{119}Sn spectra of these complexes are typical of triphenyl(IV) compounds having pentacoordinated tin atom, *viz* with three phenyl groups in the equatorial plane of trigonal bipyramide and two further ligands in its apical positions. Such arrangement can be realized, in principle, by three ways[10–12]: either by simple coordination according to the equation:

$$(C_6H_5)_3SnA + D \rightarrow [DSn(C_6H_5)_3A] \qquad (A)$$

(A = 4 X—$C_6H_4COO^{(-)}$ anion, D = molecule of the coordinating solvent), or by coordination and subsequent substitution of the anion A by the molecule D according to the equation:

$$(C_6H_5)_3SnA + 2\,D \rightarrow [D_2Sn(C_6H_5)_3]^+ + A^- \qquad (B)$$

or by the process:

$$2\,(C_6H_5)_3SnA + 2\,D \rightarrow [D_2Sn(C_6H_5)_3]^+ + [(C_6H_5)_3SnA_2]^- \qquad (C)$$

In the complexes studied by us it is obviously possible to exclude the two ionic structures (Eqs (*B*) and (*C*)). The first of them (*B*) would necessitate the presence of free 4-substituted anions which – in comparison with esters of the acids – show generally the $\delta(^{13}C)_{(COO)}$ values shifted downfield by 10–15 ppm[5]. The small upfield shifts (about 2 ppm) found by us for $\delta(^{13}C)_{(COO)}$ of the donor–acceptor complexes of the compounds studied disagree with the idea of free anions. The other possible ionic structure (Eq. (*C*)) contains tin atoms with two different coordination spheres, which would have to be manifested by the presence of two signals in the ^{119}Sn NMR spectra, and again this disagrees with experiment. Thus it can be concluded that the triphenyltin(IV) 4-substituted benzoates dissolved in the coordinating solvents studied form molecular complexes with donor–acceptor bonds formed by non-bonding electron pair of the donor atom in the coordinating solvent and bonding orbitals of the tin atom. In the *trans*-trigonally bipyramidal arrangement of the coordination sphere of the central atom the three phenyl groups are located in the

equatorial plane, the apical positions being occupied by one molecule of the coordinating solvent and the 4-substituted benzoate group. Molar ratio 1 : 1 of the complexes corresponds logically to this arrangement. It should be noted here that analogous molecular complexes of triphenyltin(IV) trifluoroacetate with various donor molecules (molar ratio 1 : 1) were recently prepared by Srivastava and Singh[13], and a similar complex of bis(triphenylstannyl) chromate in dimethyl sulphoxide was proved by ^{1}H, ^{13}C, ^{119}Sn NMR and IR spectra in our previous communication[14].

Thus formation of donor–acceptor complexes in the coordinating solvents (in contrast to deuteriochloroform) brings about a substantial change in composition of the particles in the solution. The decisive effect of the character of solvent on the ^{13}C and ^{119}Sn NMR spectral parameters of the tin atom and its closest surroundings must be understood as a reflection of structural changes in this part of the molecule. The formation of the complexes causes no distinct structural changes in the benzoate part of the molecule. Less distinct solvent effects on the $\delta(^{13}C)$ chemical shifts of this part of the molecule are due obviously to changed polarity of the triphenylstannyl group after interaction with the solvent molecule. Structure of the complexes does not depend on nature of the X substituents of the benzoate group, their effect being only manifested by polar effects in the molecule.

The donor–acceptor interaction causes – first of all – a perceptible increase of total electron density of the tin atom, which is manifested by distinct upfield shifts of $\delta(^{119}Sn)$. The electron density at the central atom of the complex depends, of course, on the character of both the donor and the acceptor. Therefore, the upfield shifts of $\delta(^{119}Sn)$ are more distinct in hexadeuteriodimethyl sulphoxide than in pentadeuteriopyridine (dimethyl sulphoxide forms stronger complexes than pyridine with triorganyltin(IV) compounds)[15] and increase with increasing acceptor ability of the benzoate group which is directly proportional to the acceptor ability of the X substituent. Consequently, the sign of the correlation coefficients ϱ of the dependences $\Delta\delta(^{119}Sn)$ *vs* σ_p must be opposite in the two the solvent types.

Increasing electron density at the tin atom increases also the *s* character of bonding orbitals Sn—$C_{(i)}$ which is manifested by an increase in the values of $^{1}J(^{119}Sn^{13}C)$ coupling constants. In other words, every decrease in $\delta(^{119}Sn)$, *i.e.* increase in the total electron density, causes an increase in $^{1}J(^{119}Sn^{13}C)$, as it is documented by negative values of α coefficients of Eq. (*1*) (Table III). The different sensitivity of changes of the $^{1}J(^{119}Sn—^{13}C)$ coupling constants depending on $\delta(^{119}Sn)$ (Table III) resp. on σ_p (Table IV) is connected with the change in the type of the hybrid orbitals of the tin atom taking part in Sn—$C_{(i)}$ bonds[2].

The structural changes due to the coordination of a solvent molecule to the central tin atom also cause changes at the carbon atoms of the three adjacent phenyl groups. The $\delta(^{13}C)_{(i)}$ chemical shifts are greater by about 4–5 ppm for the compounds measured in the coordinating solvents than those found in deuteriochloroform. In our opinion, this difference is due to increased contribution of the $(p-d)\,\pi$ inter-

action of Sn—C(phenyl) for which the planar arrangement of triphenylstannyl groups in the complex is favourable. The increased transfer of π-electron density from the phenyl nuclei to the vacant orbitals of tin atom also agrees with the changes of values of chemical shifts of the other carbon atoms of this group and, *inter alia*, also with the decrease of the difference $\delta(^{13}C)_{(p)} - \delta(^{13}C)_{(m)}$ as a measure of the total π-electron density in the phenyl nucleus. The differences in the character of hydrogen atoms which can be found in the ^1H NMR spectra[16,17] can be considered a direct consequence of the changes caused by the coordination in the carbon skeleton of the phenyl ring.

From the data given thus follows unambiguously that the ^{13}C and ^{119}Sn NMR spectral parameters of the compounds studied are affected markedly by the solvent type used. This fact can cause substantial and stuctural changes of the compounds present in the solution. The substituents in the benzoate anion have minor effects and affect to a lesser extent the electron density at the acceptor centre. In any case they will not affect substantially the composition and structure of the compounds in solution, their participation being manifested only to a lesser extent in strength of the donor–acceptor connection.

REFERENCES

1. Holeček J., Handlíř K., Nádvorník M., Lyčka A.: J. Organometal. Chem. *258*, 147 (1983).
2. Holeček J., Nádvorník M., Handlíř K., Lyčka A.: J. Organometal. Chem. *241*, 177 (1983).
3. Lyčka A., Šnobl D., Handlíř K., Holeček J., Nádvorník M.: This Journal *46*, 1383 (1981).
4. Maciel G. E., Natterstad J. J.: J. Chem. Phys. *42*, 2427 (1965).
5. Breitmeier E., Voelter W.: ^{13}C NMR *Spectroscopy*, p. 165. Verlag Chemie, Weinheim 1974.
6. Memory J. D., Wilson N. K.: NMR of *Aromatic Compounds*, p. 116. Wiley, New York 1982.
7. Kleinpeter E., Borsdorf R.: ^{13}C NMR *Spektroskopie in der Organischen Chemie*, p. 114. Akademie-Verlag, Berlin 1981.
8. Görmar G., Radeglia R., Scharm E., Schulz M.: J. Prakt. Chem. *325*, 333 (1983).
9. Epstein L. M., Ashkinadze L. D., Shubina E. S., Kravtsov D. N., Kazitsyna L. A.: J. Organometal. Chem. *228*, 53 (1982).
10. Hulme R.: J. Chem. Soc. *1963*, 1524.
11. Crowe A. J., Smith P. J., Harrison P. G.: J. Organometal. Chem. *204*, 327 (1981).
12. Aslanov L. A., Attiya W. M., Ionov V. M., Permin A. B., Petrosyan V. S.: J. Struct. Chem. *18*, 884 (1977).
13. Srivastava T. N., Singh J.: Indian J. Chem., Sect. A *22A*, 128 (1983).
14. Handlíř K., Holeček J., Nádvorník M., Lyčka A.: This Journal *49*, 1497 (1984).
15. Gutmann V.: *Coordination Chemistry in Non-Aqueous Solution*, p. 18. Springer-Verlag, Wien 1968.
16. Sau A. C., Carpino L. A., Holmes R. R.: J. Organometal. Chem. *197*, 181 (1980).
17. Sau A. C., Holmes R. R.: J. Organometal. Chem. *217*, 157 (1981).

Translated by J. Panchartek.