^{13}C AND ^{119}Sn NMR SPECTRA OF SOME MONOPHENYLTIN(IV) COMPOUNDS

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The ^{13}C and ^{119}Sn NMR spectra of some monophenyltin(IV) compounds in solution of non-coordinating (CDCl$_3$) and coordinating ((CD$_3$)$_2$SO) solvents have been studied. From the values of $\delta(^{119}Sn)$, $^1J(^{119}Sn, ^{13}C)$ and additional ^{13}C NMR parameters the coordination numbers of the central tin atom and the shapes of coordination polyhedra around the tin atom have been evaluated.

Introduction

In a series of our previous papers[1-7] values of parameters of ^{13}C and ^{119}Sn NMR spectra of numerous groups of tri- and diorganotin(IV) compounds and their complexes of the type $R_nSnX_{4-n} \cdot xD$ (where R is organic substituent n-butyl, vinyl, phenyl or benzyl, X is the polar group, D is an equivalent of the unidentate Lewis base, n = 2 or 3, x = 0 - 3) were analysed in order to find relations between their structures and these NMR spectra parameters. From this analysis we have concluded that for the qualitative description of the geometry of coordination polyhedra around Sn atom (or at least a skeleton of R_nSn), it is sufficient to use two parameters - the chemical shifts $\delta(^{119}Sn)$, which have immediate relationship to the number of partners of central tin atom (it

determines the coordination number), and the coupling constants $^1J(^{119}Sn, {}^{13}C)$, which are linear functions of magnitude of bonding angles C–Sn–C (angles θ)[8-11]. Recently[12] we have attempted to find at least the partial answer to the question, if analogous ^{119}Sn and ^{13}C NMR spectra parameters are also suitable for the prediction of the structure of monoorganotin compounds. It is shown that the values of $\delta(^{119}Sn)$ and $^1J(^{119}Sn, {}^{13}C)$ are of primary importance also in these cases for finding the determination coordination number of central tin atom. We must modify the work procedure to analyse those parameters irrespective of specification of monoorganotin(IV) compounds, which consist in the presence of only one Sn–C bond. For a complete description of structure of a monoorganotin(IV) compound, ^{13}C NMR parameters as well as NMR parameters of other nuclei are very useful. The aim of this work is to find if the results presented in paper[12] have a more general validity.

Results and Discussion

The values of ^{13}C and ^{119}Sn NMR parameters of the compounds studied in this paper are given in Table I. The number of $\delta(^{119}Sn)$ values (within the intervals of 25 ppm) of compounds measured in this paper as well as of data for other monophenyltin(IV) compounds obtained from literature[13-25], is plotted in Fig. 1 for the coordination number values of 4 - 7.

From Table I and from Fig. 1 it can be seen that the values of $\delta(^{119}Sn)$ are shifted upfield with an increasing coordination number of the central tin atom like in the tri- and diphenyltin(IV) compounds[1,7] and, in fact in all organotin compounds. But the range of the $\delta(^{119}Sn)$ values characteristic of appropriate coordination numbers are relatively broad and are not mutually separated from one another, contrary to the situation in tri- and diphenyltin(IV) compounds. The dependence of distribution of $\delta(^{119}Sn)$ values of monophenyltin(IV) compounds on the coordination number of central tin atom is very similar to that in mono(n-butyl)tin(IV) compounds[12]. We can see this fact from the existence of mutual linear dependence of $\delta(^{119}Sn)$ parameters (Fig. 2). The sets of $\delta(^{119}Sn)$ data for monophenyl- and mono(n-butyl)tin(IV) compounds (PhSn resp. BuSn), which differ only in the quality of organic substituents were obtained from this paper and from Ref.[12] We can describe the linear correlation in the following analytic form

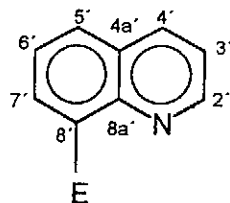$$\delta(^{119}Sn)(PhSn) = 1.053 \cdot \delta(^{119}Sn)(BuSn) - 60.673$$
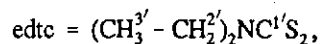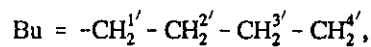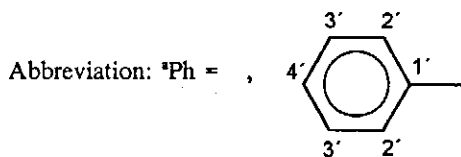
$$N = 12 \tag{1}$$

$$r = 0.989$$

The existence of very broad ranges of $\delta(^{119}Sn)$ values of the same coordination numbers of monophenyltin(IV) compounds (and probably in all monoorgano-tin(IV) compounds) and of their partial overlap is caused, in addition to the

Table I ¹³C and ¹¹⁹Sn NMR parameters of monophenyltin(IV) compounds I - XIV

Compound[a] (Solvent)	$\delta(^{119}Sn)$ ppm	$\delta(^{13}C)$, ppm / $^nJ(^{119}Sn, ^{13}C)$, Hz				Other
		C(1)	C(2)	C(3)	C(4)	
I. PhSnCl₃	-61.3	135.87	133.88	130.35	133.18	
(CDCl₃)		(1121.2)	(77.43)	(125.6)	(25.6)	
	-509.2	156.08	133.85	128.56	129.23	
((CD₃)₂SO)		(1629.8)	(80.4)	(141.6)	(26.2)	
II. PhSnBr₃	-227.2	137.75	133.25	129.94	132.74	
(CDCl₃)		(969.2)	(77.5)	(117.1)	(24.4)	
III. PhSnI₃	-699.9	134.77	130.26	128.95	132.04	
(CDCl₃)		(734.9)	(74.4)	(100.8)	(21.9)	
IV. PhSnI₂Cl	-469.2	137.05	132.62	129.41	132.35	
(CDCl₃)		(837.2)	(76.2)	(107.6)	(20.3)	
V. PhSn(SBu)₃	+95.0	138.72	135.21	129.01	134.41	36.17(1')
(CDCl₃)		(641.8)	(52.8)	(73.2)	(16.1)	27.74(2')
						21.54(3')
						13.47(4')
VI. PhSn(SBu)₂Cl	(b)	137.01	134.87	128.82	130.46	36.17(1')
(CDCl₃)		(697.8)	(55.9)	(74.3)	(b)	27.74(2')
						21.54(3')
						13.47(4')
VII. PhSn(edtc)Cl₂	-352.8	141.75	133.96	129.16	131.31	(c)
(CDCl₃)		(b)	(83.8)	(124.3)	(29.4)	194.42(1')
						52.15(2')
						11.91(3')
VIII. PhSn(edtc)₂Cl	-648.3	156.01	131.33	128.07	128.74	196.70(1')
(CDCl₃)		(1260.2)	(89.9)	(129.8)	(26.0)	51.10(2')
						11.87(3')

Pejchal V. et al./Sci. Pap. Univ. Pardubice Ser. A 2 (1996) 35-46

37

Table I   Continued

Compound[a] (Solvent)	$\delta(^{119}\text{Sn})$ ppm	$\delta(^{13}\text{C})$, ppm / $^{n}J(^{119}\text{Sn}, {}^{13}\text{C})$, Hz				Other
		C(1)	C(2)	C(3)	C(4)	
IX. PhSn(edtc)Br$_2$ (CDCl$_3$)	-480.2	141.38 (b)	133.71 (b)	129.01 (114.8)	129.95 (b)	195.48(1') 51.95(2') 11.94(3')
X. PhSn(edtc)$_2$Br (CDCl$_3$)	-704.1	155.66 (1234.5)	130.71 (91.2)	127.86 (127.2)	128.69 (24.7)	(c) 196.38(1') 51.07(2') 11.77(3')
XI. PhSn(edtc)$_3$ (CDCl$_3$)	-806.5	156.63 (1307.7)	130.28 (88.0)	127.34 (131.8)	127.84 (26.3)	198.90(1') 49.65(2') 11.56(3')
XII. PhSn(oxin)$_2$Cl (CDCl$_3$)	-448.7	143.40 (b)	134.38 (b)	128.48 (b)	130.61 (b)	(d)
XIII. PhSn(txin)$_2$Cl (CDCl$_3$)	-325.8	(b)	(b)	(b)	(b)	(b)
XIV. PhSn(acac)$_2$Cl (CDCl$_3$)	-580.6	146.08 (1625.3)	134.32 (71.2)	128.25 (131.1)	129.31 (42.0)	(e)

Abbreviation: [a]Ph =

Bu = $-CH_2^{1'} - CH_2^{2'} - CH_2^{3'} - CH_2^{4'}$,

edtc = $(CH_3^{3'} - CH_2^{2'})_2 NC^{1'}S_2$,

E = O, resp. S,

acac = $CH_3^{3'}CO^{2'}CH_2^{1'}CO^{2'}CH_3^{3'}$

oxin or txin =
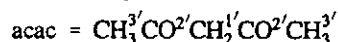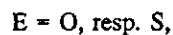
[b] not found, [c]measured in situ, [d]143.55(C-2'), 121.49(C-3'), 135.86(C-4'), 129.24(C-4a), 114.27(C-5'), 129.71(C-6'), 114.18(C-7'), 154.78(C-8'), 140.48(C-8a), [e] 101.95, 101.89(C-1'), 195.61, 194.41,(C-2'), 27.74(C-3')
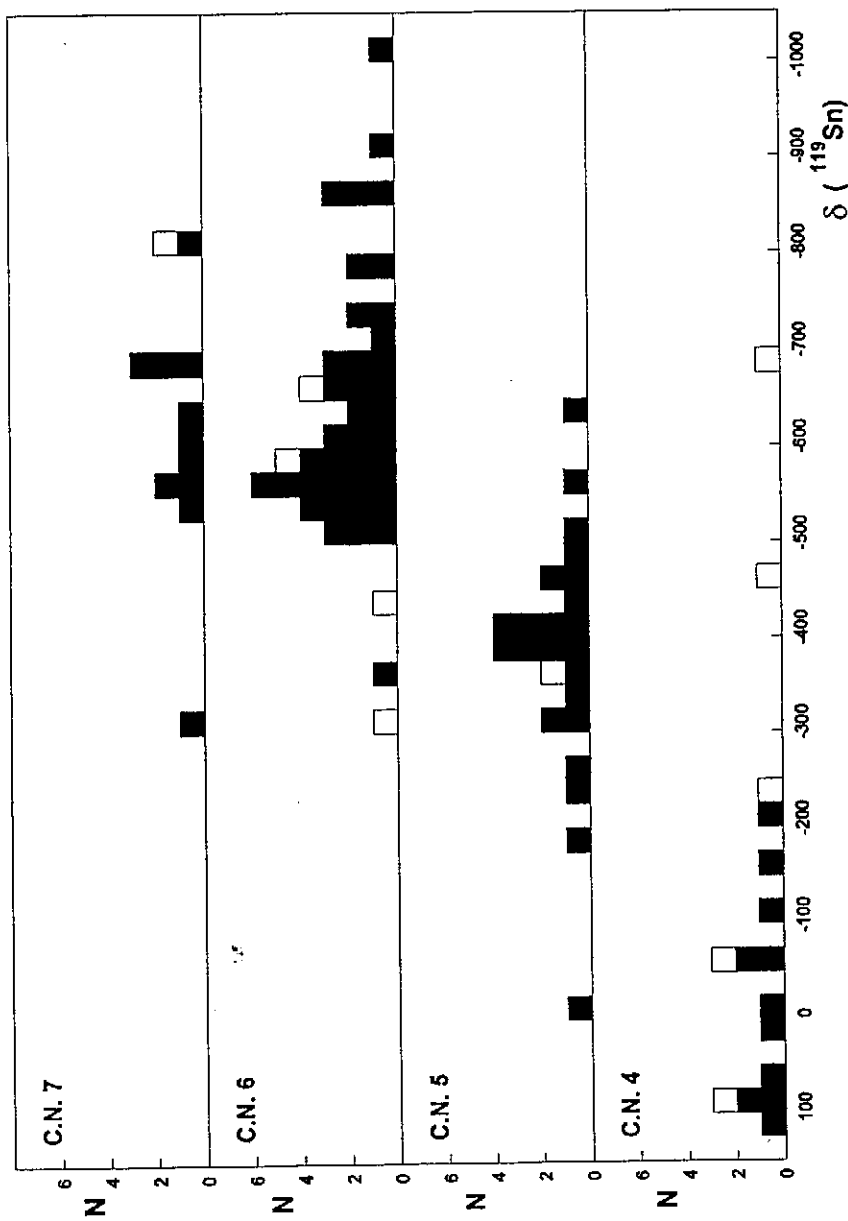
Fig. 1 The $\delta(^{119}Sn)$ values of monophenyltin(IV) compounds (intervals of 25 ppm) for coordination numbers 4 - 7: N = number of $\delta(^{119}Sn)$ values; C, N = coordination number; □ - data from this paper, ■ - literature data

coordination, also by other effects. These effects are of secondary importance in tri- and diorganotin(IV) compounds and they are overlapped by the influence of coordination and are only included in inner narrow ranges of $\delta(^{119}Sn)$ values

characteristic for the group of organotin(IV) compounds with the same coordination number of central tin atom[1-4].

Nevertheless, in the first approximation and with the use of results published in paper[12], correlation (1) and Fig. 1, we can consider the range of values $\delta(^{119}\text{Sn})$ to be characteristic of tetracoordinated compounds. This range extends from +125 to -225 ppm. Monophenyltin(IV) compounds with coordination numbers five have relatively wide range of occurence from -175 to -600 ppm, those with coordination number six from -300 to -800 ppm and heptacoordinated compounds have relatively narow range from -500 to -800 ppm.
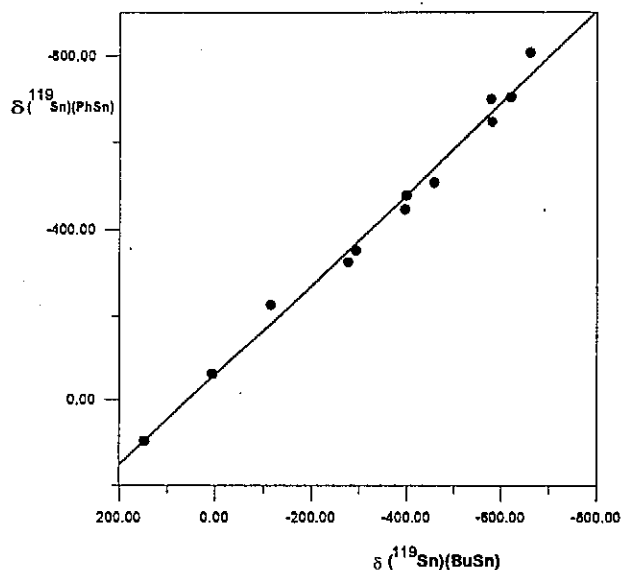

Fig. 2 The mutual dependence of $\delta(^{119}\text{Sn})$ values of mono(n-butyl)- and monophenyltin(IV) compounds

Therefore, it is evident that the application of $\delta(^{119}\text{Sn})$ values to the prediction of the coordination arrangement around the central tin atom in monophenyltin(IV) compounds (and probably in other monoorganotin(IV) compounds as well) must be careful, especially within the range where the $\delta(^{119}\text{Sn})$ values for different coordination numbers mutually overlap.

The uncertainties in the evaluation of the coordination number of central tin atom in monophenyltin(IV) compounds using the parameters of $\delta(^{119}\text{Sn})$ can be reduced by application of some parameters of ^{13}C NMR spectra.

The $\delta(^{119}\text{Sn})$ chemical shift of compound I in non-coordinating solvent (deuteriochloroform) is -61.3 ppm, while this value is shifted about 447.9 ppm upfield ($\delta(^{119}\text{Sn})$ = -509.2 ppm) in coordinating solvent (hexadeuteriodimethyl sulfoxide) into a typical region of monophenyltin(IV) compounds with the

coordination number of central tin atom equal to six. At the same time the value of coupling constant $^1J(^{119}Sn, {}^{13}C)$ increases as well. The change in both parameters is caused by the existence of the equilibrium

$$PhSnCl_3 + (CD_3)_2SO \rightleftharpoons PhSnCl_3.2(CD_3)_2SO \tag{2}$$
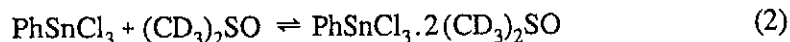
shifted predominantly towards to product, where the originally tetrahedral molecule $PhSnCl_3$ forms one possible isomers of pseudooctahedral complex $PhSnCl_3.2(CD_3)_2SO$ (it is impossible to distinguish between the isomers of this complex on the basis of the values of ^{13}C and ^{119}Sn parameters at the present state of knowledge.).

In the series of compound I - III, the $\delta(^{119}Sn)$ values are shifted substantially upfield. Simultaneously, the values of $^1J(^{119}Sn, {}^{13}C)$ decrease remarkably in this series. Therefore, it is evident that the upfield shift of $\delta(^{119}Sn)$ values in compounds II and III is not associated with an increasing coordination of the central tin atom because in such a case both parameters should increase. We assume that the observed increase in $\delta(^{119}Sn)$ parameters is due to the so-called "heavy atom effect"; its impact overlaps all other effects (unlike in the compounds Ph_3SnX or Ph_2SnX_2 where X = Br or I)[1,7] including the effect of coordination, as it can be seen from Fig. 3. The coordination number of central tin atom in compounds II and III is four as it is in compound I where the coordination number four is visible from $\delta(^{119}Sn)$ value. As both $\delta(^{119}Sn)$ and $^1J(^{119}Sn, {}^{13}C)$ parameters change only slightly with temperature and concentration in deuteriochloroform solutions, we cannot expect a significant self-association of compounds I - III. Therefore, in solution of nonpolar (non-coordinating) solvents these compounds (and obviously also compound IV exist in the form of simple tetrahedral molecules. No change of coordination in compounds II - IV on replacing the non-coordinating solvent ($CDCl_3$) by a coordinating one ($(CD_3)_2SO$) was found, because these are not sufficiently soluble in an excess of coordinating solvents even at temperatures near the boiling point of solvent.

Tetrahedral coordination of the tin atom can be assigned also to the simple molecules of compounds V and VI. Their $\delta(^{119}Sn)$ values in deuteriochloroform belong indicatively into the region of $\delta(^{119}Sn)$ values characteristic of monophenyltin(IV) compounds with the four-coordinated tin atom. The influence of coordination on $\delta(^{119}Sn)$ values with an elimination or radical repression of "heavy atom effect" was studied in series of $PhSnX_n(chel)_{3-n}$ type (X = Cl, resp. Br, chel = edtc, oxin, txin and acac). In the case of compounds VII - IX, both the values of $\delta(^{119}Sn)$ and $^1J(^{119}Sn, {}^{13}C)$ increase with increasing parameters n (i.e., increasing number of chelating edtc groups), giving thus the evidence for an increasing coordination number of central tin atom. The upfield shift of $\delta(^{119}Sn)$ values with increasing coordination number of central tin atom are not quite regular. The reason for it could lie in the fact that the values of $\delta(^{13}C)$ in the $-CS_2$ group in edtc ligands

Pejchal V. et al./Sci. Pap. Univ. Pardubice Ser. A 2 (1996) 35-46

41

increase with increasing number n, as a result of an increasing bonding strength of the chelate bonding of CS_2 group to the tin atom[29]. For compounds VII - XI, the chemical shifts $\delta(^{13}C(1'))$ of the edtc ligands lie between those of organic ester $(C_2H_5)_2NC(S)SC_2H_5$ $(\delta(^{13}C(1') = 194.5$ ppm)[30], which we consider a prototype of the monodentate $-CS_2$ group, and the $(C_2H_5)_2NCS_2^{(-)}$ $(\delta(^{13}C(1') = 209.0$ ppm)[30], which serves as prototype of its purely bidentate function. It can be deduced that in all the compounds studied, the edtc ligands are bonded anisobidentately to the tin atom, i.e. by one strong and one weaker Sn-S bond. The latter grows stronger with increasing coordination number of central tin atom. Compounds VII and IX (coordination number of central tin atom being five) have the shapes of distorted trigonal bipyramides, compounds VIII and X (with hexacoordinated tin atom) are pseudooctahedral complexes and compound XI, which has the coordination number of central tin atom seven, has the shape of distorted pentagonal bipyramide. This shape of molecule of compound XI was verified using X ray diffraction study[31].
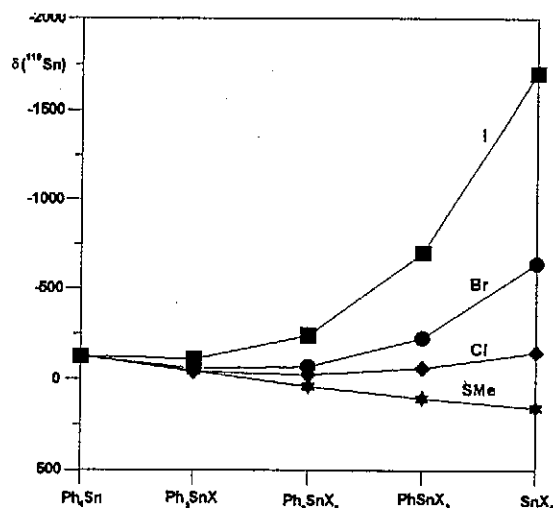

Fig. 3 The dependence of $\delta(^{119}Sn)$ values on the parameter n for compounds of the type Ph_nSnX_{4-n} where X = Cl, Br, I or SMe. (The $\delta(^{119}Sn)$ values of monophenyltin(IV) compounds were taken from literature[26-28])

Out of $PhSnCl_n(chel)_{3-n}$ chelating complexes, we succeeded in preparation and ^{13}C and ^{119}Sn NMR measurement of compounds XII - XIX only, i.e. compounds with n = 1. All these compounds occur as pseudooctahedral complexes according to $\delta(^{119}Sn)$ and $^1J(^{119}Sn, ^{13}C)$ values. Compound XIII has the pseudooctahedral shape too even though this compound has slightly smaller values of relevant ^{13}C and ^{119}Sn NMR parameters. Reasons, which were discissed in the work[12,29], consist in a somewhat different nature of compounds

42

with the S-Sn bond. This fact supporsts anomal course of curve of compounds $Ph_nSn(SMe)_{4-n}$ (Fig. 3).

Experimental

Compounds I - III, V, VII - XII, and XIV were prepared according to published procedures[10-17]. Compound IV was synthesized by reacting monophenyltin(IV) trichloride with sodium iodine in acetone in molar ratio 1:2. Compound VI was prepared by reaction of monophenyltin(IV) trichloride with n-butanethiole and sodium methanolate in methanol. Compound XIII was obtained by reaction of monophenyltin(IV) trichloride with sodium thiooxinate in methanol.

The basic physical and analytical data of the newly prepared products are summarized in Table II.

Table II   Analytical and physical data for compounds IV, VI and XIII

Compound	Formula M.w.	Found / (Calculated)				M.p. (b.p.) °C / Torr
		%C	%H	%Sn	%Others	
IV.	$C_6H_5SnI_2Cl$	13.92	0.91	24.79	I: 54.35	(129- 131/2.5)
$PhSnI_2Cl$	485.06	(14.86)	(1.04)	(24.47)	(52.33)	
					Cl: 6.16	
					(7.31)	
VI.	$C_{14}H_{23}SnS_2Cl$	42.10	5.24	27.13	S: 15.99	(128-133/1.5)
$PhSn(SBu)_2Cl$	409.6	(41.76)	(5.62)	(29.01)	(15.64)	
					Cl: 7.92	
					(8.66)	
XIII.	$C_{24}H_{17}SnN_2S_2Cl$	51.82	3.17	22.07	S: 11.06	251-254
$PhSn(txin)_2Cl$	551.68	(52.26)	(3.08)	(21.54)	(11.61)	
					N: 4.49	
					(5.08)	
					Cl: 7.18	
					(6.43)	

The ^{119}Sn (134.29 MHz) and ^{13}C (90.566 MHz) NMR spectra were recorded at 300 K on a Bruker AMX 360 spectrometer equipped with 5 mm multinuclear tuneable probe and X32 computer using the UXNMR software (Version 940501.3). Compounds were measured in $CDCl_3$ or $((CD_3)_2SO))$, their

concentrations being 5 - 30%. The ^{13}C chemical shifts were reffered to appropriate signals of solvents and recalculated to δ-scale ($\delta(^{13}C)$ = 77.00 (CDCl$_3$); 39.60 ((CD$_3$)$_2$SO)). The ^{119}Sn chemical shifts were reffered to external neat (CH$_3$)$_4$Sn (δ = 0.0) placed in a coaxial capillary.

Conclusion

From the results discussed above it can be concluded that the knowledge of the parameters of ^{13}C and ^{119}Sn NMR spectra in monophenyltin(IV) compounds, especially of $\delta(^{119}Sn)$ chemical shift and $^1J(^{119}Sn, ^{13}C)$ coupling constant and their combination is very important for the prediction of the geometry of coordination polyhedra of these compounds in their solutions. Contrary to tri- and diphenyltin(IV) compounds, and, in fact, to generally all tri- and diorganotin(IV) compounds, the coordination numbers in monophenyltin(IV) compounds cannot be estimated only from the $\delta(^{119}Sn)$ and $^1J(^{119}Sn, ^{13}C)$ values without the knowledge of further ^{13}C NMR spectral parameters. This fact supports the validity of results published in our previous paper[12], dealing with an interplay of ^{13}C and ^{119}Sn NMR spectral parameters in mono(n-butyl)tin(IV) compounds.

Acknowledgements

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45

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