

ANNEXURE

PREPARATION AND INFRARED AND ^{13}C , ^{17}O , AND ^{119}Sn
NMR SPECTRA OF SOME SUBSTITUTED DI- AND TRI(1-BUTYL)TIN
PHENOXYACETATES AND PHENYLTHIOACETATES

Jaroslav HOLEČEK^a, Karel HANDLÍŘ^a, Antonín LYČKA^b, T. K. CHATTOPADHYAY^c,
B. MAJEE^c and A. K. KUMAR^c

^a Department of General and Inorganic Chemistry,
Institute of Chemical Technology, 532 10 Pardubice, Czechoslovakia,

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

^c Department of Chemistry, University of North Bengal,
734 430 Darjeeling, India

Received June 4th, 1985

The paper describes preparation and basic physical and chemical properties of a group of substituted di- and tri(1-butyl)tin(IV) phenoxyacetates and phenylthioacetates of the general formula $(\text{R}_x\text{C}_6\text{H}_5-x\text{ECH}_2\text{CO}_2)_n\text{Sn}(\text{i-C}_4\text{H}_9)_{4-n}$, where R = H, 2-Cl, 4-Cl, 2-CH₃, and 2-OCH₃, E means oxygen or sulphur atoms, n = 1 or 2, and x = 1 or 2. From IR spectral data, ^{13}C , ^{17}O , and ^{119}Sn NMR spectra, and from other physico-chemical methods, conclusions are drawn about structure of the compounds in solid state and in solutions of coordinating (hexamethylphosphoric triamide) and non-coordinating solvents (chloroform, carbon tetrachloride, carbon disulphide, benzene). In solid state the tri(1-butyl)tin(IV) compounds form polymeric chains with bidentate bridge carboxylic groups. In non-coordinating solvents these compounds are present as isolated pseudo-tetrahedral molecules, whereas in hexamethylphosphoric triamide they form complexes with one solvent molecule, the central tin atom exhibiting the *trans*-trigonally bipyramidal coordination. The di(1-butyl)tin(IV) compounds form, both in solid state and in non-coordinating solvents, monomeric particles containing bidentate chelate carboxylic groups. In hexamethylphosphoric triamide they form complexes with octahedral coordination around the tin atom containing monodentate carboxylic groups and the butyl groups at *trans* position. In none of the cases studied evidence was obtained for interaction of the oxygen or sulphur atoms of $\text{C}_6\text{H}_5\text{ECH}_2$ group with the tin atom.

An unusual increase is observed in production of organotin compounds during the past few years. This fact is particularly due to their biocidal properties and the consequent application to the pest control, ecology problems, veterinary medicine and human medicine, etc. For these purposes especially suitable are the compounds type $\text{R}_n\text{SnX}_{4-n}$, where R means an organic substituent and X is a polar group (anion of an acid). Out of the most frequently wanted are such compounds whose biocidal properties are due not only to the R_nSn group but also to the X group, because in these cases the effects are mutually combined and complemented. The organotin(IV) compounds of this type in which the X group is formed by phosphate or its organo-

-analogues and sulphur analogues were studied in more detail both from physical and from chemical points of view¹⁻⁴.

In the context of a systematic study of synthesis, properties and structure of organotin(IV) compounds, we prepared a series of substituted di- and tri(*i*-butyl)tin(IV) phenoxyacetates and phenylthioacetates of the general formula $(R_xC_6H_{5-x}ECH_2.CO_2)_nSn(1-C_4H_9)_{4-n}$, where R stands for H, 2-Cl, 4-Cl, 2-CH₃, and 2-OCH₃, E means oxygen or sulphur atom, n is 1 or 2, and x is 1 or 2. Biocidal properties of phenoxyacetic acid and its derivatives as well as those of phenylthioacetic acid are sufficiently known⁵. They were also reexamined in combination with the organotin(IV) component⁶. There is no doubt, either, that structure of these compounds is significantly connected with their biocidal properties and/or ways of their practical application⁷.

EXPERIMENTAL

All the compounds studied (Table I) were prepared in the yields of 78 to 92% by azeotropic dehydration of the stoichiometric mixture of the respective phenoxyacetic or phenylthioacetic acid and bis tri(*i*-butyl)stannyl oxide or di(*i*-butyl)stannyl oxide in benzenic solution. The products obtained by crystallization of the concentrated solutions were recrystallized from a mixture of benzene and petroleum ether (60–80°C). Table I summarizes the results of elemental analyses and melting points. The molecular masses of the compounds were determined by cryoscopy in benzene or by osmometry in carbon tetrachloride. In both the solutions, the values measured correspond to monomeric character of the compounds. The infrared spectra were measured with a Perkin-Elmer apparatus type 684 in solid state (KBr disc or suspension in paraffine oil) and in solution (carbon tetrachloride, carbon disulphide) in the range from 4 000 to 200 cm⁻¹. The cells used were made of KBr (4 000–300 cm⁻¹) and polyethylene (600–200 cm⁻¹). The ¹³C, ¹⁷O, and ¹¹⁹Sn NMR spectra were measured with a JNM-FX 100 apparatus (JEOL, Japan) at 25.047, 13.50, and 37.14 MHz, respectively. The ¹³C and ¹¹⁹Sn NMR spectra were measured in solutions of deuteriochloroform and hexamethylphosphoric triamide at 300 K (if not otherwise stated), the ¹⁷O NMR spectra were measured in saturated solutions in chloroform at 330 K. The chemical shifts $\delta(^{13}C)$ are related to a suitable signal of the solvent ($\delta(C^2HCl_3) = 77.00$ ppm, $\delta((CH_3)_6N_3PO) = 36.00$ ppm) and transformed to the δ scale, the $\delta(^{17}O)$ and $\delta(^{119}Sn)$ values are related to external neat deuterium oxide and tetramethylstannane, respectively. The details of measurement and interpretation of the NMR spectra were described earlier^{8,9}.

RESULTS

Preparation and Identification of Compounds

All the compounds investigated (prepared by esterification of the respective acids with bis tri(*i*-butyl)stannyl oxide or di(*i*-butyl)stannyl oxide) are colourless crystalline solids with well-defined melting points (usually relatively low). Their analyses results agree well with theory (Table I). Moreover, the compounds were identified by their IR and ¹³C and ¹¹⁹Sn NMR spectra (see below). All the data obtained agree with the

TABLE I
Chemical analysis and melting points of compounds I–IV

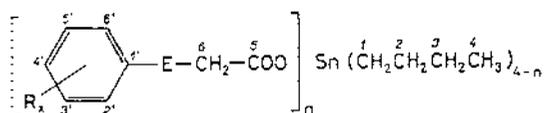
No	Compound	Elemental analysis (calculated/found), %				Melting point, °C
		C	H	Sn	others	
<i>Ia</i>	$C_6H_5OCH_2COOSn(C_4H_9)_3$	54.59	7.59	26.79		53.0–54.0
		54.45	7.77	26.90		
<i>Ib</i>	$2-CH_3C_6H_4OCH_2COOSn(C_4H_9)_3$	55.84	8.07	25.97		70.5–71.5
		55.41	7.97	26.07		
<i>Ic</i>	$4-ClC_6H_4OCH_2COOSn(C_4H_9)_3$	50.42	7.08	24.65	7.75 ^a	74.0–76.0
		50.51	6.99	24.95	7.45	
<i>Id</i>	$2-ClC_6H_4OCH_2COOSn(C_4H_9)_3$	50.75	7.03	24.53	7.57 ^a	68.0–68.5
		50.51	6.99	25.95	7.45	
<i>Ila</i>	$(C_6H_5OCH_2COO)_2Sn(C_4H_9)_2$	54.09	6.14	21.98		133.0–134.5
		53.86	6.03	22.18		
<i>Ilb</i>	$(2-CH_3C_6H_4OCH_2COO)_2Sn(C_4H_9)_2$	55.76	6.42	21.37		112.0–114.0
		55.44	6.44	21.07		
<i>Ilc</i>	$(4-ClC_6H_4OCH_2COO)_2Sn(C_4H_9)_2$	47.71	5.07	19.69	11.93 ^a	125.0–126.0
		47.72	5.00	19.65	11.74	
<i>Ile</i>	$(2,4-Cl_2C_6H_3OCH_2COO)_2Sn(C_4H_9)_2$	42.97	4.38	17.94	20.83 ^a	167.0–170.0
		42.83	4.19	17.64	21.07	
<i>IIf</i>	$(2-CH_3OC_6H_4OCH_2COO)_2Sn(C_4H_9)_2$	52.32	6.23	20.08		120.0–122.0
		52.46	6.10	19.94		
<i>III</i>	$C_6H_5SCH_2COOSn(C_4H_9)_3$	52.80	7.36	26.10	6.87 ^b	63.0–67.0
		52.54	7.50	25.96	7.01	
<i>IV</i>	$(C_6H_5SCH_2COO)_2Sn(C_4H_9)_2$	50.69	6.12	21.15	11.03 ^b	88.0–89.0
		50.81	5.69	20.92	11.30	

^a Cl; ^b S.

TABLE II
The band frequencies of carboxylic and phenoxymethyl groups in compounds I–IV (cm^{-1})

Compound	Solid phase				Solution			
	$\nu_a(\text{COO})$	$\nu_s(\text{COO})$	$\nu_a(\text{COC})$	$\nu_s(\text{COC})$	$\nu_a(\text{COO})$	$\nu_s(\text{COO})$	$\nu_a(\text{COC})$	$\nu_s(\text{COC})$
<i>Ia</i>	1 587 vs	1 421 s	1 243 s 1 220 sh	1 085 s	1 690 vs 1 665 vs	1 358 m 1 340 s	1 245 s 1 218 s	1 085 s
<i>Ib</i>	1 577 vs	1 413 s	1 243 vw 1 224 vs	1 085 s	1 690 vs 1 666 vs	1 358 w 1 340 s	1 245 vs 1 225 vs	1 085 s
<i>Ic</i>	1 585 vs	1 415 vs	1 245 sh 1 225 vs	1 075 vs	1 690 vs 1 663 vs	1 358 sh 1 342 s	1 243 s 1 225 vs	1 078 vs
<i>Id</i>	1 583 vs	1 417 vs	1 235 vs	1 082 vs	1 690 vs 1 667 vs	1 355 w 1 340 s	1 245 m 1 228 vs	1 080 vs
<i>IIa</i>	1 615 vs	1 416 vs	1 240 sh 1 217 vs	1 083 vs	1 637 vs	1 407 vs	1 240 s 1 218 vs	1 090 vs
<i>IIb</i>	1 553 vs	1 416 vs	1 245 sh 1 228 vs	1 075 vs	1 640 vs	1 405 vs	1 247 vs 1 226 vs	1 080 vs
<i>IIc</i>	1 623 vs	1 420 s	1 245 vs 1 220 m	1 082 vs	1 645 vs	1 405 vs	1 247 s 1 230 vs	1 082 vs
<i>IId</i>	1 608 vs	1 418 vs	1 235 vs 1 220 sh	1 080 vs	1 643 vs	1 405 s	1 232 vs 1 220 sh	1 080 vs
<i>IIe</i>	1 615 vs	1 412 s	1 255 vs 1 228 vs	1 073 m 1 055 vs	1 640 vs	1 405 s	1 255 vs 1 215 vs	1 070 vs 1 055 s
<i>III</i>	1 575 vs	1 370 vs			1 665 vs 1 655 vs	1 340 sh 1 327 vs		
<i>IV</i>	1 592 vs	1 370 vs			1 612 vs	1 360 vs		

presumed constitution which is schematically represented by the formula:



where R is the respective substituent of the phenyl ring, E means an oxygen or sulphur atom, and n, x are 1 or 2. The small numbers in the formula denote the carbon atoms for assignment of the signals in ^{13}C NMR spectra (Table IV).

Infrared Spectra

All the spectral bands were found at practically identical wavenumber values in solid phase and in solutions of the compounds. This is true especially of the frequencies due to the 1-butyl group and most frequencies due to the phenyl ring. These bands as well as those of the other *i.e.* X-sensitive vibrations of the phenyl ring (out of which some are identical with the vibrations of the C—O—C or C—S—C grouping), vibrations of carboxylic group, vibrations of substituents in the phenyl ring, of the methylene group in the phenoxyacetates or phenylthioacetates, and of the Sn—O and/or Sn—C bonds were assigned on the basis of comparison of the spectra of the compounds studied with those of the original acids, their methyl esters, further di- and tri-(1-butyl)tin(IV) compounds, and literature data ¹⁰⁻¹³.

The bands of valence vibrations of carboxylic group, those due to Sn—C bonds, and the bands of phenoxyethyl or phenylthiomethyl group are fundamentally important for discussion of structure of the compounds studied and shape of the coordination polyhedron around the tin atom. The other bands, although they have their informative value (serving for identity proof of the compounds studied), are of minor importance for the discussion of structure (Table II).

Dominant bands of the spectra of tri(1-butyl)tin(IV) phenoxyacetates (*Ia-Ic*), both in solid state and in solvents, are intensive broad absorption bands ν_a and ν_s of carboxylic group and ν_a and ν_s of phenoxyethyl group ($\nu_a(\text{COC})$ is frequently denoted as the vibration of phenyl-oxygen bond, $\nu_s(\text{COC})$ being ascribed to the O—CH₂ bond vibration)¹³. In contrast to the $\nu_a(\text{COC})$ and $\nu_s(\text{COC})$ bands, whose position in the regions of 1 245–1 218 and 1 085–1 075 cm⁻¹, respectively, does not depend on the phase state of the sample (the intensity changes of these bands in solid state and in solution are connected with the presence of rotamers, as it is shown below), the position as well as number of $\nu_a(\text{COO})$ and $\nu_s(\text{COO})$ bands depend markedly on the phase state. In solid state, $\nu_a(\text{COO})$ and $\nu_s(\text{COO})$ are found in the regions of 1 587–1 577 and 1 421–1 413 cm⁻¹, respectively ($\Delta\nu \sim 170$ cm⁻¹). In solution, on the contrary, $\nu_a(\text{COO})$ is found as a pair of bands in the region of 1 690–1 663 cm⁻¹, the pair of $\nu_s(\text{COO})$ bands being shifted to the region of 1 358

to 1340 cm^{-1} . The ν_a and ν_s values in the solid state are characteristic for a bridge bidentate carboxylic group, the same values in solutions correspond to a monodentate carboxylic group¹⁴. The coupling of bands in solution is obviously due to the presence of two rotamers (*s-cis* and *s-trans*), the magnitude of splitting of the bands ($\sim 20\text{ cm}^{-1}$) being comparable with the similar phenomenon observed with organic¹⁵ and organosilicon¹⁶ phenoxycetates.

The deformation vibrations of carboxylic group are less distinct than the valence vibrations. The scissoring vibration is found as a band of medium intensity in the region of $712\text{--}700\text{ cm}^{-1}$, the out-of-plane and in-plane deformation vibrations forming weak bands in the regions of $615\text{--}603$ and $515\text{--}500\text{ cm}^{-1}$, respectively. The $\nu_a(\text{SnC})$ and $\nu_s(\text{SnC})$ vibrations make themselves felt as weak spectral bands at $580\text{--}570$ and $530\text{--}520\text{ cm}^{-1}$, respectively. The $\nu(\text{SnO})$ vibration is ascribed (in accordance with ref.¹⁰) to a band of medium to weak intensity in the region of $286\text{--}268\text{ cm}^{-1}$.

The bands due to valence vibrations of carboxylic and phenoxymethyl groups are also dominant in the spectra of di-(1-butyl)tin(IV) phenoxycetates (*IIa*–*IIf*). The vibration bands of phenoxymethyl group $\nu_a(\text{COC})$ and $\nu_s(\text{COC})$ are found in spectra of both the solid phase and solution in the regions of $1255\text{--}1215$ and $1090\text{--}1080\text{ cm}^{-1}$, respectively, *i.e.* practically the same as those of the tri(1-butyl)-tin(IV) compounds. Again, the position of the bands of valence vibrations of carboxylic group depends (even though to a lesser extent) on the phase state, *i.e.* whether the sample is crystalline or in solution. In solid state the $\nu_a(\text{COO})$ bands are found in the region of $1623\text{--}1608\text{ cm}^{-1}$ (except the compound *IIb*) and $\nu_s(\text{COO})$ at 1420 to 1416 cm^{-1} ($\Delta\nu \sim 200\text{ cm}^{-1}$). In carbon tetrachloride solutions, $\nu_a(\text{COO})$ is shifted to higher wavenumbers ($\sim 1640\text{ cm}^{-1}$), whereas $\nu_s(\text{COO})$ is slightly shifted to lower wavenumbers ($\sim 1405\text{ cm}^{-1}$) ($\Delta\nu \sim 235\text{ cm}^{-1}$). The positions of bands of the compounds in solid state are typical of bidentate chelate function of carboxylic group (with compound *IIb* it is necessary to presume a bridge arrangement of COO group), in solutions the situation is between the monodentate and chelate functions of carboxylic group. The other vibrations of carboxylic group lie in the regions identical with those of compounds *Ia*–*Id* (an intensive band of the scissoring vibration in the region of $750\text{--}720\text{ cm}^{-1}$, weak bands of out-of-plane and in-plane deformation vibrations at $625\text{--}610$ and $512\text{--}495\text{ cm}^{-1}$, respectively). The vibrations of Sn–C bonds are manifested as weak bands in the regions close to those of the deformation vibrations of carboxyl ($610\text{--}580$ and $532\text{--}495\text{ cm}^{-1}$, respectively). The $\nu(\text{SnO})$ vibrations are ascribed to the bands of medium to weak intensity in the region of $280\text{--}270\text{ cm}^{-1}$.

The infrared spectra of the two phenylthioacetates *III* and *IV* can be compared to a considerable extent with their oxygen analogues (compounds *Ia* and *IIa*), taking, of course, as self-evident that the intensive $\nu(\text{COC})$ bands disappear and the position of X-sensitive bands is changed, too. It is important to find that $\nu_a(\text{COO})$ and $\nu_s(\text{COO})$

(and, hence, also their difference) have similar values as those of the oxygen analogues. Therefore, the same conclusions can be made about their structure inclusive of the existence of two rotamers of compound *III*. Slight shifts of $\nu_s(\text{COO})$ and $\nu_a(\text{COO})$ to the region of lower wavenumbers observed with compounds *III* and *IV* (as compared with *Ia* and *Ila*) are connected with the more distinct donor properties of the $\text{C}_6\text{H}_5\text{S}\cdot\text{CH}_2\text{CO}_2^-$ anion as compared with $\text{C}_6\text{H}_5\text{OCH}_2\text{CO}_2^-$, which is confirmed, *inter alia*, also by values of the dissociation constants of their conjugated acids¹⁷.

NMR Spectra -

The parameters of ^{13}C , ^{17}O , and ^{119}Sn NMR spectra of compounds *I–IV* are given in Tables III and IV. From the tables it can be seen that the deuteriochloroform solutions exhibit a single signal at 300 K in the ^{119}Sn spectrum; the number of signals in the ^{13}C spectrum corresponds to the number of magnetically non-equivalent carbon atoms in the structural formula suggested for the respective compound.

The chemical shifts $\delta(^{119}\text{Sn})$ of the tri(1-butyl)tin(IV) compounds in deuteriochloroform solutions have the values 125.5 to 132.9 ppm, the coupling constants $^1J(^{119}\text{Sn}^{13}\text{C})$ of these compounds vary within the limits from 350.3 to 352.8 Hz.

TABLE III
Chemical shifts $\delta(^{119}\text{Sn})$ and $\delta(^{17}\text{O})$ and coupling constants $^nJ(^{119}\text{Sn}^{13}\text{C})$ of compounds *I–IV*

Compound	$\delta(^{119}\text{Sn})^a$, ppm	$\delta(^{17}\text{O})^b$, ppm/ $w_{1/2}^c$, Hz	$^nJ(^{119}\text{Sn}^{13}\text{C})^d$, Hz		
			n = 1	n = 2	n = 3
<i>Ia</i>	130.9	258/700	352.2	20.8	64.7
<i>Ia</i> ^e	– 61.3		511.5	29.0	80.6
<i>Ib</i>	127.7		352.0	20.8	64.7
<i>Ic</i>	132.9		350.3	20.8	64.7
<i>Id</i>	132.2		351.6	20.8	64.7
<i>Ila</i> ^f	– 117.4	249/900	549.3	36.0	100.1
<i>Ila</i> ^e	– 298.3		811.8	34.2	140.4
<i>Ilb</i>	– 117.1		548.1	36.6	101.3
<i>Ilc</i>	– 114.4		545.7	36.0	100.1
<i>Ile</i>	– 110.5		544.4	36.6	102.5
<i>Ilf</i>	– 119.7		556.6	36.6	105.0
<i>III</i>	125.5	276/500	352.8	20.8	67.1
<i>IV</i>	– 135.8	272/1 000	559.7	34.8	102.5

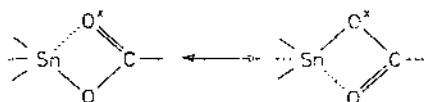
^a 300 K, deuteriochloroform; ^b 330 K, chloroform, saturated solution, ± 3 ppm; ^c the signal half-width, $\pm 10\%$; ^d $^4J(^{119}\text{Sn}^{13}\text{C}) < 5$ Hz; ^e solution in hexamethylphosphoric triamide; ^f 220 K, two signals (– 116.4 and – 200.9 ppm) with the integral intensity ratio of 4 : 1.

TABLE IV
Chemical shifts $\delta(^{13}\text{C})$ of compounds I–II' in deuteriochloroform at 300 K

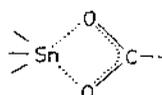
Compound	$\delta(^{13}\text{C})$, ppm									
	$\text{C}_{(1)}$	$\text{C}_{(2)}$	$\text{C}_{(3)}$	$\text{C}_{(4)}$	$\text{C}_{(5)}$	$\text{C}_{(6)}$	$\text{C}_{(5')}$	$\text{C}_{(2')}$	$\text{C}_{(3')}$	$\text{C}_{(4')}$
Ia	16.52	27.53	26.85	13.45	173.45	65.32	157.90	114.33	129.15	120.96
Ia ^a	18.89	27.62	26.69	13.24	170.56	65.97	158.67	114.08	128.46	119.54
Ib ^b	16.52	27.63	26.90	13.50	173.79	65.84	156.30	126.91	130.66	120.72
Ic	16.57	27.58	26.85	13.50	173.21	65.65	156.59	115.70	129.05	125.88
Id ^c	16.60	27.53	26.85	13.45	172.77	66.28	153.71	122.81	130.27	121.64
IIa	25.44	26.17	26.02	13.21	178.18	64.72	157.37	114.19	129.20	121.35
IIa ^a	28.54	26.59	26.06	13.19	172.61	65.34	158.23	114.18	128.65	120.02
IIb ^d	25.39	26.26	26.07	13.26	178.33	65.25	155.81	127.00	130.86	121.15
IIc	25.73	26.36	26.17	13.40	177.79	65.21	156.15	115.70	129.30	126.52
IIc ^e	25.87	26.50	26.26	13.44	177.11	66.39	152.30	124.23	130.42	127.00
II _f	25.53	26.17	25.97	13.21	177.79	65.83	<i>f</i>	<i>f</i>	111.75	<i>g</i>
III	16.52	27.58	26.90	13.50	174.13	36.70	136.07	128.66	128.66	125.93
IV	25.19	26.12	26.02	13.21	179.25	35.72	135.00	<i>h</i>	<i>h</i>	126.33

^a Solution in hexamethylphosphoric triamide; ^{b–h} further values $\delta(^{13}\text{C})$, ppm: ^b 126.37 ($\text{C}_{(5')}$), 110.87 ($\text{C}_{(6')}$), 16.18 ($\text{C}_{(\text{CH}_3)}$); ^c 127.25 ($\text{C}_{(5')}$), 131.21 ($\text{C}_{(6')}$); ^d 126.32 ($\text{C}_{(5')}$), 110.73 ($\text{C}_{(6')}$), 15.98 ($\text{C}_{(\text{CH}_3)}$); ^e 127.40 ($\text{C}_{(5')}$), 114.50 ($\text{C}_{(6')}$); ^f 149.23 or 146.84; ^g 122.08 or 120.28 ($\text{C}_{(4')}$) and ($\text{C}_{(5')}$), 113.50 ($\text{C}_{(6')}$), 55.46 ($\text{C}_{(\text{OCH}_3)}$); ^h 128.86 or 128.71.

Both these parameters, which are significant for evaluation of structure, possess the values typical of quasitetrahedral arrangement around the tin atom in this type of compounds¹⁸. With the di(1-butyl)tin(IV) compounds, the values of chemical shifts $\delta(^{119}\text{Sn})$ and coupling constants $^1J(^{119}\text{Sn}^{13}\text{C})$ (in deuteriochloroform solutions) vary within the limits from -110.5 to -135.8 ppm and from 544.4 to 559.7 Hz, respectively, which values (with the di(1-butyl)tin(IV) compounds) are typical of a pentacoordinated tin atom^{19,20}. Thus it is obvious that in compounds *II* and *IV* in chloroform solutions (with regard to monomeric character of these compounds), phenoxyacetate and phenylthioacetate must act as multi-donor chelate-forming ligands. With selected representatives of the tri(1-butyl)tin(IV) compounds (compounds *Ia* and *III*) and di(1-butyl)tin(IV) compounds (compounds *IIa* and *IV*) we could measure the chemical shifts $\delta(^{17}\text{O})$. In each of the cases, one signal was only found for the two oxygen atoms of carboxylic group, its position being approximately in the middle of the interval containing the signals of the two oxygen atoms of carboxyl group of organic esters (no signal due to oxygen atom of phenoxymethyl group was found in compounds *Ia* and *IIa*; the reason obviously lies in its large width, because even in the case of methyl phenoxyacetate the half-width of the signal of oxygen atom of the phenoxymethyl group is roughly twice as large as that of both oxygen atoms of carboxyl group). Similar phenomenon was encountered also with other tri- and di(1-butyl)tin(IV) carboxylates and was explained in ref.⁹ by a rapid exchange of the oxygen atom in the COOSn fragment in the NMR time scale as follows:



which, from the point of view of the NMR time scale, is equivalent to the arrangement:



and indicates a bonding affinity of the tin atom of di- and tri(1-butyl)tin(IV) compounds to both the oxygen atoms of the carboxyl group. Hence, it seems likely that both the oxygen atoms contribute (even though to different extents) to the bonding interactions of the carboxyl group with the central tin atom. The donor-acceptor bond of the oxygen atom of carbonyl group, of course, is much weaker than a simple covalent SnO bond in the $\text{Sn}-\text{O}-\text{C}$ grouping and thus the carboxyl group acts, in this respect, as an asymmetrical bidentate chelate-forming ligand in the two types of compounds. Such a role of carboxylic group in the di(1-butyl)tin(IV) compounds is not surprising, after all, it is in accordance with results of IR spectra. The asym-

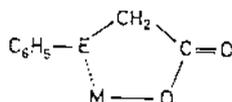
metrical chelate connection with the very weak donor-acceptor interaction of the carbonyl oxygen atom and the tin atom was also proved recently in the case of molecular crystals of some sterically hindered triphenyltin(IV) carboxylates^{21,22}. The degree of asymmetry obviously depends on the strength of the donor-acceptor connection, *i.e.* on the donor ability of oxygen atom of carbonyl group and the acceptor ability of the central tin atom. Thus it can be expected that it will depend significantly on the character of the organic residue bound to the carboxyl group as well as on the character and number of organic substituents and polar groups bound to the tin atom. With the tri(1-butyl)tin(IV) compounds the interaction of the oxygen atom of carbonyl group with the tin atom obviously is very weak, and it will not distinctly affect the electronic, bonding, and geometrical relations in the other parts of the molecule; consequently, these compounds behave as tetracoordinated ones in accordance with the ¹³C and ¹¹⁹Sn NMR and IR spectra. The stronger Lewis acidity of the di(1-butyl)tin(IV) compounds causes a more distinct interaction of the tin atom with oxygen atom of carbonyl group, which results in the parameters of the ¹³C and ¹¹⁹Sn NMR spectra being consistent with a pentacoordinated tin atom. If, however, the idea of asymmetrical four-membered chelate connection of carboxyl group with tin atom is considered to be justified, it will not be improper to characterize the number of the partners bound to the tin atom in tri- and di(1-butyl)tin(IV) compounds by the coordination numbers five and six, respectively. The idea of asymmetrical chelate connection thus brings certain troubles with determination of the coordination number of the central tin atom, on the contrary, however, it allows a unified and logical explanation of apparently contradictory experimental facts.

In both the types of compounds the tin atom is distinctly incompletely saturated in its coordination, which is indicated by marked differences in the ¹³C and ¹¹⁹Sn NMR spectral parameters of compounds *Ia* and *IIa* when going from deuteriochloroform solutions to hexamethylphosphoric triamide. The distinct shift of the $\delta(^{119}\text{Sn})$ values to higher field and the increase in $^1J(^{119}\text{Sn}^{13}\text{C})$ and $\delta(^{13}\text{C}_{(1)})$ are due to formation of much stronger complexes with one and two solvent molecules, resp., and with trans-trigonally bipyramidal¹⁸ and trans-octahedral^{19,20} (with respect to the C₍₁₎ atoms) coordination, respectively, of the central tin atom. In these complexes the original chelate function of carboxyl group disappears, which is manifested in a down-field shift of the $\delta(^{13}\text{C}_{(5)})$ value²³. The magnitude of these changes correlates with the strength of the original chelate complexes.

The ¹¹⁹Sn NMR spectrum of compound *IIa* measured at 220 K exhibits, besides the original signal (at 300 K) a new one at higher field (~ -200 ppm). We have not enough data for interpretation of this signal yet; it could only be stated that this signal is due to a new particle with a higher coordination number at the tin atom (probably six) and with a stronger connection of the central tin atom with the coordination partners.

DISCUSSION

A characteristic structural feature usually found in molecules and crystals of phenoxacetates and phenylthioacetates of metals (transition metals in particular) is a five-membered chelate cycle



(M stands for the metal atom) in which an important part is played by the donor-acceptor intramolecular connection of the E atom and the central metal atom M^{24} . In the structures of the compounds studied by us this feature is not observed.

At room temperature, the compounds studied behave like most tri- and diorganotin(IV) carboxylates. The tri(1-butyl)tin(IV) compounds form polymers in solid phase, the quasi-planar $(1-C_4H_9)_3Sn$ groups (their perfect planarity would necessitate the absence of $\nu_s(SnC)$ from the IR spectra) being mutually connected by the oxygen atoms of carboxyl groups. Then the $O-Sn(1-C_4H_9)_3 \cdots O$ grouping has a shape of slightly deformed *trans*-trigonal bipyramid. In non-coordinating solvents these compounds are present in the form of isolated molecules with deformed tetrahedral structure. The deformation is caused by the heterogeneity of the coordination sphere and by the weak interaction of the carbonyl oxygen atom with the central tin atom. In coordinating solvents, stronger complexes are formed with one solvent molecule and with *trans*-trigonally bipyramidal coordination sphere around the tin atom. The di(1-butyl)tin(IV) compounds form, obviously in both solid state and non-coordinating solvents, chelate complexes with considerably asymmetrical function of the two oxygen atoms of carboxyl group and, hence, with a deformed octahedral structure. In hexamethylphosphoric triamide the complexes formed contain two molecules of the solvent. These complexes only contain the monodentate carboxylic groups, they are octahedral, and according to the high $^1J(^{119}Sn^{13}C)$ values they contain the 1-butyl groups in *trans* position.

In none of the structures given we could observe an intramolecular connection of the oxygen or sulphur atom of $C_6H_5ECH_2$ group with the central tin atom. Of course, intermolecular interactions of oxygen atoms of $C_6H_5OCH_2$ groups with tin atoms of other molecules (with formation of dimers or higher associates) cannot be completely excluded. The parameters of the second signal of the ^{119}Sn NMR spectrum which was found with compound *Ia* at low temperatures at higher field (Table III, footnote *f*) could indicate formation of such associates²⁵. No analogous phenomenon was observed with the similar compound *IV*, which could be connected with the well-known reluctance of the sulphur atom (in contrast to the oxygen atom) to form additional donor-acceptor connections²⁶.

REFERENCES

1. Blunden S. J., Hill R., Gillies D. G.: *J. Organometal. Chem.* **270**, 39 (1984).
2. Lecat J. L., Deraud M.: *Polyhedron* **2**, 1087 (1983).
3. Clark H. C., Jain V. K., Mehrotra R. C., Singh B. P., Srivastava G., Birchall T.: *J. Organometal. Chem.* **279**, 385 (1985).
4. Nasser F. A. K., Zuckerman J. J.: *J. Organometal. Chem.* **244**, 17 (1983) and the references quoted therein.
5. Pillmoor J. B., Gaunt J. K.: *Progr. Pestic. Biochem.* **1**, 147 (1981).
6. Bublitz D. E.: U.S. Pat. 3 598 849; *Chem. Abstr.* **75**, 118408r (1971).
7. Crowe A. J., Smith P. J., Atassi G.: *Inorg. Chim. Acta* **93**, 179 (1984).
8. Holeček J., Nádvořník M., Handlíř K., Lyčka A.: *J. Organometal. Chem.* **241**, 177 (1983).
9. Lyčka A., Holeček J.: *J. Organometal. Chem.* **294**, 179 (1985).
10. Honning W. D., Zuckerman J. J.: *J. Organometal. Chem.* **178**, 111 (1979) and the references quoted therein.
11. Forel M. T., Carrigon-Lagrange C., Gemin J., Josieu M. L.: *J. Chim. Phys.* **60**, 1047 (1963).
12. Geisler H., Kriegsmann H.: *J. Organometal. Chem.* **11**, 85 (1968).
13. Horák M., Papoušek D.: *Infračervená spektra a struktura molekul*, p. 439. Academia, Prague 1976.
14. Deacon G. B., Phillips R. J.: *Coord. Chem. Rev.* **33**, 227 (1980).
15. Oki M., Hirota M.: *Bull. Chem. Soc. Jap.* **34**, 374 (1961).
16. Pola J., Jakoubková M., Papoušková Z., Chvalovský V.: *This Journal* **42**, 1540 (1977).
17. Behangel O.: *J. Prakt. Chem.* **114**, 299 (1926).
18. Nádvořník M., Holeček J., Handlíř K., Lyčka A.: *J. Organometal. Chem.* **275**, 43 (1984).
19. Mitchell T. N.: *J. Organometal. Chem.* **59**, 189 (1973).
20. Smith P. J., Tupčiauskas A. P.: *Ann. Rep. NMR Spectrosc.* **8**, 291 (1978).
21. Swisher R. G., Vollano J. F., Chandrasekhar V., Day R. O., Holmes R. R.: *Inorg. Chem.* **23**, 3147 (1984).
22. Vollano J. F., Day R. O., Rau D. N., Chandrasekhar V., Holmes R. R.: *Inorg. Chem.* **23**, 3153 (1984).
23. Kleinpeter E., Borsdorf R.: *¹³C-NMR-Spectroscopie in der organischen Chemie*, p. 114. Akademie-Verlag, Berlin 1981.
24. O'Reilly H., Smith G., Kennard C. H. L.: *Inorg. Chim. Acta* **90**, 637f (1984) and the references quoted therein.
25. Davies A. G., Hawari J. A. A., Hua-de P.: *J. Organometal. Chem.* **251**, 203 (1983).
26. Zubieta J. A., Zuckerman J. J.: *Progr. Inorg. Chem.* **24**, 252 (1978) and the references quoted therein.

Translated by J. Pancharček.

