SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
5 (1999)

SUBSTITUTED TRIBUTYLTIN(IV) PHENOLATES

Milan NÁDVORNÍK[a1] and Vladimír PEJCHAL[b]
[a]Department of General and Inorganic Chemistry, University of Pardubice,
CZ-532 10 Pardubice
[b]Research Institute of Organic Syntheses, CZ-532 18 Pardubice

Received October 26, 1998

Substituted tributyltin(IV) phenolates of general formula (1-C_4H_9)$_3$SnOC_6H_4R, where R is H(I), 4-CH_3(II), 4-OCH_3(III), 4-$NHCH_3$(IV), 4-$COCH_3$(V), 4-$NHCOCH_3$(VI), 4-Cl(VII), 4-Br(VIIa), 4-NO_2(IXa), 2-NO_2(IXa'), 4-$COOC_2H_5$(X) and 4-CN(XI), as well as selected polysubstituted tributyltin(IV) phenolates: 2,4-diBr(VIIIb), 2,4,6-triBr(VIIIc), 2,4-diNO_2(IXb) and 2,4,6-triNO_2(IXc) have been synthesized and studied by means of ^{1}H, ^{13}C and ^{119}Sn NMR specroscopy.

According to the values of $\delta(^{119}Sn)$ chemical shifts, all the compounds prepared form — in solutions of non-coordinating solvent ($CDCl_3$) — simply pseudotetrahedral molecules with co-ordination number at tin atom equal to four.

The complexes of tributyltin(IV) phenolates with one molecule of solvent are formed in solutions of coordinating solvent (hexadeuteriodimethyl sulfoxide). These complexes form trans-trigonal bipyramidal molecules with butyl groups in equatorial positions, coordination number at tin atom equal to five and the C–Sn–C angle 118 – 122 ° according to values of $^1J(^{119}Sn, ^{13}C)$.

The values of the chemical shift $\delta(^{119}Sn)$ correlate (with exception those for compounds VIIIc, IXc and XI) with Taft's constants σ_I (N = 13, r = 0.927).

---

[1] To whom correspondence should be addressed.

Introduction

Organotin compounds represent a kind of organometallic compounds, which are extensively studied and produced and utilized in chemical industry [1]. Surprisingly, the group of triorganotin(IV) phenolates has been studied quite rarely. Their synthesis has been known since the sixties and seventies. Obviously, at that time the present methods of the structural research were not available, and the structure of the triorganotin(IV) phenolates was not studied. In general, triorganotin(IV) phenolates are potentially applicable e.g. as efficient fungicides or disinfectants.

At first, the aim of the present paper was to prepare the selected group of tributyltin(IV) phenolates, mainly 4-substituted, as well as polysubstituted ones, at second, to characterize their physico-chemical properties and study their structure by means of multinuclear magnetic resonance in solutions with both non-coordinating and coordinating solvents.

Experimental

The solvents used were dried by the standard methods described elsewhere [2].

Tributyltin(IV) chloride (pure, Lachema Brno) was distilled at reduced pressure (bp. 118 – 119 °C/4 hPa) before use.

Bis(tributyltin(IV)) oxide was prepared by alkaline hydrolysis of tributyltin(IV) chloride; the tributyltin(IV) hydroxide intermediate was dehydrated by azeotropic distillation with benzene and the product was distilled at reduced pressure (bp. 185 °C/4 hPa, n_D^{20} = 1.4868, Ref. [3] 1.4860).

Tributyltin(IV) methoxide was prepared by reaction of tributyltin(IV) chloride with sodium methoxide in methanol (bp. 110 – 116 °C/4 – 5 hPa, Ref. [1] 90 °C/0.1 Torr).

The substituted phenols used for the reactions were of "purum" purity grade and were used as delivered (Lachema Brno or Lancaster Synthesis). 4-(N-methylamino)phenol was used as the sulfate (METOL, pure, Lachema Brno).

All the other chemical substances used were of "purum" purity grade at least.

The Schlenk flasks technique and setup for the purification and distribution of argon as inert gas were used for preparation of substituted tributyltin(IV) phenolates. The inert gas was deoxygenated with BTS catalyst and dried with molecular sieve NALSIT 4 (Lachema Brno).

The compounds studied were synthesized according to some of following chemical reactions:

A) reaction of bis(tributyltin(IV)) oxide and phenol in benzene with removal of formed water by azeotropic distillation

$$2\ R\text{–}C_6H_4\text{–}OH + (Bu_3Sn)_2O \Rightarrow 2\ R\text{–}C_6H_4\text{–}OSnBu_3 + H_2O$$

B) conversion of tributyltin(IV) chloride by sodium phenolate prepared *in situ* (by reaction of sodium methoxide and phenol) in methanol

$$R\text{–}C_6H_4\text{–}OH + CH_3ONa + Bu_3SnCl \Rightarrow R\text{–}C_6H_4\text{–}OSnBu_3 + NaCl + CH_3OH$$

C) reaction of tributyltin(IV) methoxide and phenol in methanol

$$R\text{–}C_6H_4\text{–}OH + Bu_3SnOMe \Rightarrow R\text{–}C_6H_4\text{–}OSnBu_3 + MeOH$$

Determination of C, H, N elements was carried out on an EA 1108 CHN instrument (Fison's Instruments). Tin content was determined gravimetrically. Samples were decomposed in a quartz crucible with a mixture of conc. H_2SO_4 and conc. HNO_3 6:1 (v:v), followed by annealing to SnO_2 (the process was modified according to Ref. [4]).

The ^1H (360,13 MHz), ^{13}C (90,566 MHz) and ^{119}Sn (90,566 MHz) NMR spectra were measured with a Bruker AMX 360 apparatus in pulse-mode with Fourier transformation in a 5 mm zone tuneable probe and with help of an X32 computer (UXNMR software — version 940501.3). The compounds synthesized were measured in 10 – 30% solutions or saturated solutions in deuteriochloroform or hexadeuteriodimethyl sulfoxide at 300 K. The chemical shifts $\delta(^{13}C)$ were referred to the respective solvent signal and recalculed to δ scale [$\delta(^{13}C)$ = 77.0 ($CDCl_3$), 39.6 ($(CD_3)_2SO$)]. The $\delta(^1H)$ and $\delta(^{119}Sn)$ chemical shifts were referenced to the internal hexamethydisiloxane (δ = 0.05) and external tetramethylstannane (δ = 0.00), resp.

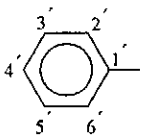
The two-dimensional spectra H,H–COSY a H,C–COSY were measured by means of pulse programs delivered by the producer of spectrometer. The H,C–COSY experiment was optimized on the coupling constant J (^{13}C, ^1H) 150 – 160 Hz and 8 – 10 Hz. The ^{119}Sn NMR spectra were measured in the so-called "inverse gate" mode with proton noise decoupling during the acquisition period.

Results and Discussion

All the chemical reactions used for preparation of the compounds studied together with their yields, compounds characterization and the results of elemental analysis of newly prepared compounds are listed in Table I.

The NMR parameters of synthesized compounds are listed in Tables II and III (^{1}H NMR) and Tables IV and V (^{13}C and ^{119}Sn NMR). In the tables the atoms of hydrogen and carbon are marked as follows

R = Bu $CH_3^{4}CH_2^{3}CH_2^{2}CH_2^{1}$ —

R = Ph 

The ^{1}H and ^{13}C NMR spectra allowed to identify the synthesized compouds and to analyze their purity. Unambiguous assignment of the ^{1}H and ^{13}C signals, especially in aromatic area of ^{1}H NMR spectra, was carried out by combination of one-dimensional and two-dimensional (H,H–COSY and H,C–COSY) NMR techniques.

The chemical shifts $\delta(^{119}Sn)$ and coupling constants $^{1}J(^{119}Sn, ^{13}C)$ were used for determination of coordination number at the tin atom and as an estimate of coordinating polyhedron geometry.

The chemical shift values $\delta(^{119}Sn)$ of synthesized compouds (110.4 – 157.3 ppm, with exception of picrate IXc — 195.6 ppm) in deuteriochloroform are typical for tributyltin(IV) compounds with the coordination number 4 at the tin atom (Ref. [12]). The coupling constants $^{1}J(^{119}Sn, ^{13}C)$ in 321.8 – 374.4 Hz range correspond with correlation equation for butyltin(IV) compounds (Ref. [13])

$$|\,^{1}J(^{119}Sn, ^{13}C)(Bu_nSn| = 9.99\theta - 746$$

to the magnitude of bond angles θ (C–Sn–C) in the range of 107 – 112°. For picrate IXc, the value of $\delta(^{119}Sn)$ found was near to the same value as for tributyltin(IV) perchlorate ($\delta(^{119}Sn)$ = 196.8 ppm in CD_3NO_2, Ref. [14]). In both above-mentioned compounds, there is probably trigonal pyramidal cation Bu_3Sn^+ with coordination number three at the tin atom.

The general upfield shift of $\delta(^{119}Sn)$ values (values from - 19.9 to 19.4 are typical for pentacoordinated tributyltin(IV) compouds [12] accompanying the change from deuterio-chloroform solutions to solutions in the coordinating solvent hexadeuteriodimethyl sulfoxide is due to formation of donor-acceptor complexes

Table I List of synthesized tributyltin(IV) phenolates $Bu_3SnOC_6H_4R$, their characterization and results of elemental analysis

R No comp.	Method of prep	yield, %	Characterization	Elemental analysis, calc./found				
				Sn	C	H	N	Ref.
H I	A	84	colourless oil bp. 205 – 210/7	31.06 30.95				5,6,7
4-CH_3 II	A	96	colourless oil	29.88 29.74				8,9
4-OCH_3 III	C	86	colourless oil bp. 152 – 4 / 0.1	28.72 28.21				10
4-$NHCH_3$ IV	B	60	pale yellow oil	28.79 28.52	55.35 55.55	8.58 8.63	3.40 3.44	
4-$COCH_3$ V	C	68	colourless solid mp. 30 – 35 (*)	27.91 27.85	56.49 56.93	8.08 8.14		
4-NH-$COCH_3$ VI	C	72	colourless solid mp. 79 – 82 (**)	26.96 26.31	54.56 54.35	8.03 8.15	3.18 3.10	
4-Cl VII	A	85	slightly yellow oil bp. 203 – 205/7	28.42 27.98				8
4-Br VIIIa	C	81	slightly yellow oil bp. 230 – 235/5–6	25.69 25.61				9
2,4-diBr VIIIb	B	89	slightly yellow oil	21.94 21.93	39.36 35.93	5.60 5.00		
2,4,6-triBr VIIIc	C	87	slightly yellow oil	19.15 18.77	34.78 33.11	4.73 4.50		
4-NO_2 IXa	A	97	yellow oil decomp. by dest.	27.72 27.42				11
2-NO_2 IXa'	A	93	yellow oil	27.72 27.12	50.49 47.36	7.31 6.82	3.27 3.77	
2,4-diNO_2 IXb	A	89	yellow oil on light get dark	25.08 24.67	45.69 46.42	6.40 6.47	5.92 6.45	
2,4,6-triNO_2 IXc	A	88	red oil	not analyzed for potentially safety hazards				
4-COO-C_2H_5 X	B	92	slightly yellow oil	29.73 29.68	54.15 48.54	8.10 7.42		
4-CN XI	C	90	slightly yellow oil	29.08 28.52	55.90 54.34	7.67 7.49	3.43 4.02	

Table I - Continued

(*) crystallized from chloroform–heptane mixture at -40 °C
(**) crystallized from chloroform–hexane mixture at - 8 °C
Most of other oily products were not distilled because of the high risk of decomposition (see IXa).
The ^{1}H- NMR spectra were used as purity criterion

Table II Chemical shifts δ(^{1}H) [ppm] of compounds studied in solutions of $CDCl_3$

Compound	H(1)	H(2)	H(3)	H(4)	H(2')	H(3')	H(4')	H(5')	H(6')	Other
I	1.18	1.57	1.30	0.86	6.64	7.05	6.62	7.05	6.64	
II	1.19	1.59	1.31	0.86	6.65	6.85	-	6.85	6.65	δ(CH_3) = 2.17
III	1.19	1.59	1.31	0.88	6.59	6.65	-	6.65	6.59	δ(CH_3) = 3.62
IV	1.18	1.58	1.32	0.87	6.40	6.54	-	6.54	6.40	δ(CH_3) = 2.65 δ(NH) = 3.38
V	1.30	1.63	1.32	0.87	6.67	7.79	-	7.79	6.67	δ(CH_3) = 2.45
VI	1.22	1.58	1.32	0.87	6.59	7.29	-	7.29	6.59	δ(CH_3) = 2.03 δ(NH) = 8.47
VII	1.21	1.58	1.31	0.86	6.59	7.04	-	7.04	6.59	
VIIIa	1.22	1.58	1.31	0.86	6.53	7.16	-	7.16	6.53	
VIIIb	1.25	1.60	1.29	0.86	-	7.50	-	7.12	6.55	
VIIIc	1.34	1.62	1.28	0.86	-	7.49	-	7.49	-	
IXa	1.32	1.63	1.34	0.87	6.65	8.07	-	8.07	6.65	
IXa'	1.30	1.62	1.30	0.87	-	7.32	6.74	6.85	7.84	
IXb	1.34	1.68	1.42	0.89	-	8.75	-	8.25	6.92	
IXc	1.48	1.68	1.35	0.90	-	8.85	-	8.85	-	
X	1.27	1.61	1.31	0.87	6.62	7.84	-	7.84	6.62	δ(CH_3) = 0.86 δ(CH_2) = 4.23
XI	1.28	1.63	1.32	0.87	6.66	7.37	-	7.37	6.66	

of the present compounds with one molecule of this solvent

$$Bu_3SnOC_6H_4R + dmso \Rightarrow Bu_3SnOC_6H_4R.dmso$$

The coupling constant values $^1J(^{119}Sn, ^{13}C)$ in the range of 431.6 – 477.9 Hz, corresponding to bond angles θ (C–Sn–C) of 118 – 122° (Ref. [13]) indicate that butyl substituents in these complexes assume equatorial positions in trans-trigonal bipyramidal arrangement of bond partners of the tin atom. The axial positions of

Table III Chemical shifts $\delta(^1H)$ [ppm] of compounds studied in solutions of dmso–d_6

Compound	H(1)	H(2)	H(3)	H(4)	H(2')	H(3')	H(4')	H(5')	H(6')	Other
I	1.16	1.67	1.39	0936	6.59	7.07	6.57	7.07	6.59	
II	1.15	1.68	1.39	0.94	6.50	6.88	-	6.88	6.50	$\delta(CH_3)$ = 2.21
III	1.20	1.74	1.42	0.97	6.60	6.72	-	6.72	6.60	$\delta(CH_3)$ = 3.69
IV	values of chemical shifts were not measured due to decomposition of compound									
V	1.11	1.52	1.31	0.84	6.50	7.70	-	7.70	6.50	$\delta(CH_3)$ = 2.39
VI	1.05	1.56	1.29	0.85	7.22	6.44	-	6.44	7.22	$\delta(CH_3)$ = 1.96 $\delta(NH)$ = 9.50
VII	1.11	1.61	1.33	0.87	6.51	7.02	-	7.02	6.51	
VIIIa	1.12	1.62	1.31	0.87	6.46	7.13	-	7.13	6.46	
VIIIb	1.18	1.68	1.36	0.91	-	7.51	-	7.15	6.53	
VIIIc	1.22	1.64	1.28	0.84	-	7.47	-	7.47	-	
IXa	1.14	1.58	1.28	0.82	6.54	7.99	-	7.99	6.54	
IXa'	1.14	1.61	1.30	0.84	-		-			
IXb	1.11	1.54	1.27	0.81	-	8.55	-	8.07	6.62	
IXc	1.12	1.53	1.27	0.84	-	8.57	-	8.57	-	
X	1.19	1.68	1.37	0.91	6.54	7.77	-	7.77	6.54	$\delta(CH_3)$ = 1.31 $\delta(CH_2)$ = 4.23
XI	1.18	1.64	1.34	0.88	6.59	7.36	-	7.36	6.59	

TBP are occupied by oxygen atom of phenolate and oxygen atom of hexadeuteriodimethyl sulfoxide.

The obtained chemical shifts $\delta(^{119}Sn)$ of the compounds in solution of deuteriochloroform correlate with values of Taft's constants σ_I. For the whole group of sixteen compounds, the following equation was found

$$\delta(^{119}Sn) = 38.5\sigma_I + 105.7 \quad N = 16 \quad r = 0.901$$

By omitting the chemical shift values given for compounds VIIIc, IXc and XI, the correlation is expressed (see Fig. 1) by equation

$$\delta(^{119}Sn) = 33.48\sigma_I + 109 \quad N = 13 \quad r = 0.927$$

In two selected groups of studied derivates (bromophenolates and nitrophenolates) together with non-substituted phenolate, it was found that the che-

Table IV ^{119}Sn and ^{13}C NMR parameters of compounds studied in $CDCl_3$

Compound	δ(^{119}Sn), ppm	δ(^{13}C), ppm \ (J(^{119}Sn, ^{13}C), Hz)			
		C(1)	C(2)	C(3)	C(4)
I	113.0	15.28 (354.9)	27.22 (20.4)	26.49 (60.6)	13.01
II	112.6	15.32 (355.5)	27.33 (20.3)	26.60 (61.1)	13.10
III	122.8	15.35 (354.3)	27.35 (20.3)	26.64 (61.4)	13.13
IV	111.2	15.19 (321.8)	27.32 (19.8)	26.59 (61.3)	13.10
V	114.0	16.29 (363.2)	27.32 (21.9)	26.56 (64.5)	13.12
VI	120.0	15.85 (346.8)	27.52 (19.7)	26.82 (61.8)	13.36
VII	123.8	15.8 (351.8)	27.45 (20.4)	26.77 (62.3)	13.29
VIIIa	123.9	15.87 (351.6)	27.47 (20.5)	26.78 (61.3)	13.33
VIIIb	137.9	16.76 (347.4)	27.59 (20.3)	26.95 (61.8)	13.51
VIIIc	150.5	17.91 (335.8)	27.54 (18.5)	26.93 (59.2)	13.45
IXa	128.8	16.38 (354.8)	27.18 (21.9)	26.34 (63.5)	12.93
IXa'	135.3	17.10 (354.1)	27.41 (20.0)	26.80 (63.7)	13.31
IXb	157.3	18.01 (350.5)	27.27 (21.8)	26.67 (65.7)	13.18
IXc	195.6	19.64 (347.1)	27.19 (20.7)	26.72 (70.8)	13.16
X	114.2	15.94 (360.7)	27.23 (21.5)	26.48 (63.2)	13.00
XI	110.4	16.60 (368.8)	27.25 (23.1)	26.40 (65.3)	13.00

Table IV - Continued

Compound	δ(^{13}C), ppm						Other
	C(1')	C(2')	C(3')	C(4')	C(5')	C(6')	
I	161.86	117.62	128.55	119.03	128.55	117.62	
II	159.48	118.85	129.17	126.46	129.17	118.85	δ(CH_3) = 19.92
III	155.59	114.04	119.57	151.93	119.57	114.04	δ(CH_3) = 54.98
IV	153.58	113.23	119.56	141.58	119.56	113.23	δ(CH_3) = 31.19
V	167.32	118.48	130.43	127.30	130.43	118.48	δ(CO) = 196.13 δ(CH_3) = 28.85
VI	158.64	119.36	121.76	129.37	121.76	119.36	δ(CO) = 168.43 δ(CH_3) = 23.76
VII	160.75	120.59	128.75	122.59	128.75	120.59	
VIIIa	161.27	121.20	131.71	109.83	131.71	121.20	
VIIIb	158.19	109.87	134.51	116.73	130.97	121.74	
VIIIc	155.17	116.75	133.67	109.61	133.67	116.75	
IXa	169.45	118.82	125.79	138.55	125.79	118.82	
IXa'	157.91	124.28	125.25	134.53	128.71	117.69	
IXb	163.42	136.99	124.18	138.84	128.77	122.22	
IXc	156.57	142.03	124.67	134.51	124.67	142.03	
X	166.32	118.58	131.08	118.99	131.08	118.58	δ(COO) = 167.33 δ(CH_3) = 13.83 δ(CH_2) = 59.50
XI	166.87	119.66	133.22	98.76	133.22	119.66	δ(CN) was not determined

mical shifts δ(^{119}Sn) correlate well with the number of bromine atoms or nitro groups in the phenols, and with their pK_A as well. The equation for chemical shifts of bromoderivates (n is number of bromine atoms in one phenol molecule) is

$$\delta(^{119}\mathrm{Sn}) = 12.62n + 112.4 \quad N = 4 \quad r = 0.998$$

$$\delta(^{119}\mathrm{Sn}) = -8.86\,\mathrm{pK_A} + 104.5 \quad N = 4 \quad r = 0.971$$

and for nitroderivates (n is number of nitro groups in one phenol molecule) is

Table V ^{119}Sn and ^{13}C NMR parameters of studied compounds in dmso–d_6

Compound	δ(^{119}Sn), ppm	δ(^{13}C), ppm \ (J(^{119}Sn. ^{13}C), Hz)			
		C(1)	C(2)	C(3)	C(4)
I	2.1	17.55 (440.4)	27.77 (25.6)	26.64 (70.0)	13.50
II	8.2	17.40 (440.4)	27.82 (25.0)	26.72 (68.2)	13.52
III	19.39	17.26 (431.6)	27.94 (25.1)	26.86 (68.1)	13.58
IV	parameters were not measured due to decomposition of compound				
V	-19.7	18.28 (473.1)	27.70 (27.1)	26.49 (68.0)	13.54
VI	-3.7	17.58 (441.7)	27.75 (26.3)	26.61 (71.3)	13.60
VII	-2.6	17.90 (463.7)	27.8 (26.9)	26.64 (72.1)	13.59
VIIIa	-7.1	17.89 (461.1)	27.75 (26.6)	26.59 (67.5)	13.52
VIIIb	-13.8	18.54 (472.4)	27.71 (27.4)	26.56 (73.7)	13.51
VIIIc	2.2	19.82 (465.8)	27.87 (25.6)	26.81 (81.2)	13.61
IXa	-18.0	18.74 (477.3)	27.89 (27.5)	26.68 (74.1)	13.59
IXa'	-11.8	18.89 (457.7)	27.74 (27.3)	26.66 (75.7)	13.54
IXb	-19.9	19.23 (472.3)	27.56 (27.9)	26.42 (76.0)	13.47
IXc	10.9	19.53 (456.6)	27.54 (28.4)	26.38 (76.1)	13.53
X	-14.4	18.32 (469.1)	27.93 (27.1)	26.74 (72.7)	13.58
XI	-5.2	18.66 (468.4)	28.13 (27.4)	26.97 (73.9)	13.79

Table V - Continued

Compound	δ(^{13}C), ppm						Other
	C(1')	C(2')	C(3')	C(4')	C(5')	C(6')	
I	163.39	116.00	128.76	119.19	128.76	116.00	
II	160.96	118.88	129.28	124.33	129.28	118.88	δ(CH_3) = 20.14
III	156.80	114.39	119.20	151.14	119.20	114.39	δ(CH_3) = 29.11
IV	parameters were not measured due to decomposition of compound						
V	not obtained	118.60	130.52	125.01	130.52	118.60	δ(CO) = 195.09 δ(CH_3) = 25.87
VI	158.64	117.99	120.94	129.96	120.94	117.94	δ(CO) = 167.26 δ(CH_3) = 23.67
VII	162.34	120.35	128.53	119.43	128.53	120.35	
VIIIa	162.83	121.07	131.36	106.73	131.36	121.07	
VIIIb	159.89	105.61	133.65	116.13	130.61	120.98	
VIIIc	157.20	116.45	133.31	105.53	133.31	116.45	
IXa	171.38	118.59	126.14	136.72	126.14	118.59	
IXa'	159.61	141.23	125.07	133.67	123.64	114.12	
IXb	166.47	132.59	124.01	138.82	128.32	122.80	
IXc	160.92	142.01	125.22	124.31	125.22	124.01	
X	166.19	119.10	131.23	116.72	131.23	119.10	δ(COO) = 169.83 δ(CH_3) = 14.38 δ(CH_2) = 59.35
XI	168.98	120.34	133.61	97.29	133.61	120.34	δ(CN) was not determined

$$\delta(^{119}\mathrm{Sn}) = 27.57n + 107.4 \quad N = 5 \quad r = 0.969$$

$$\delta(^{119}\mathrm{Sn}) = -8.59\,\mathrm{pK_A} + 195.4 \quad N = 5 \quad r = 0.986$$

The attempt to correlate all 16 chemical shift δ(^{119}Sn) values of the compounds with pK_A values of corresponding phenols was not successful; no reasonable correlation was found ($N = 16$, $r = 0.05$).

The values of characteristic quantities of phenoles (pK_A, σ_I) for the above-

mentioned correlations are listed in Table VI.

Table VI Characteristic quantities of substituted phenols used in the present work

Phenol in compound	pK_A [15]	σ_I [16]
I	9.97	0
II	10.2	-0.01
III	10.21	0.30
IV	10.2 [17,18]	0.17
V	8.05	0.30
VI	8.5 [19]	0.28
VII	9.42	0.47
VIIIa	9.34	0.47
VIIIb	7.8 [20]	0.94
VIIIc	5.9 [21]	1.41
IXa	7.16	0.67
IXa'	7.22	0.67
IXb	4.09	1.34
IXc	0.29	2.01
X	8.37 [22]	0.30
XI	7.95	0.57

Conclusion

Sixteen substituted tributyltin(IV) phenolates were synthesized and studied by means of ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. In the solutions of non-coordinating solvent ($CDCl_3$), tributyltin(IV) phenolates are formed from tetrahedrally coordinated molecules, and in the solutions of coordinating solvent (hexadeuteriodimethyl sulfoxide) trans-trigonal bipyramidal complexes of phenolate arise with one molecule of solvent and butyl groups in equatorial positions.

The chemical shifts $\delta(^{119}Sn)$ of compounds studied correlate satisfactorily with values of Taft's constants σ_I.

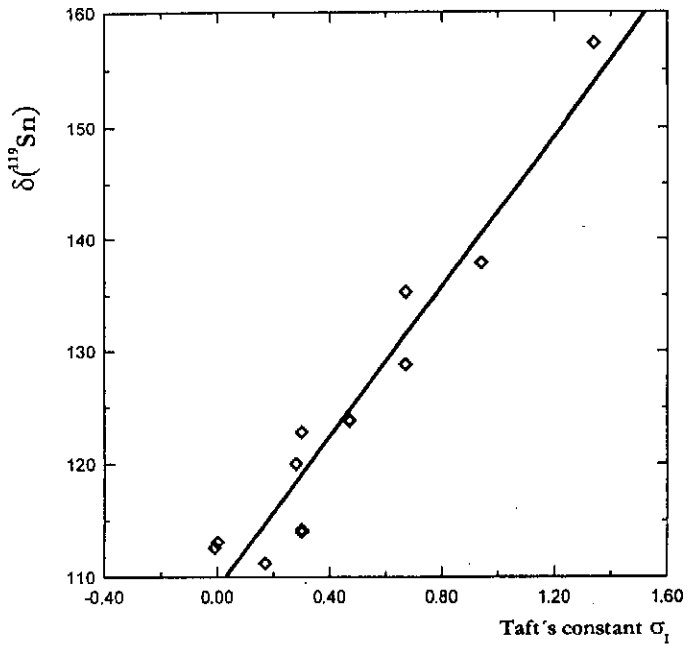


Fig. 1 Correlation of the chemical shift $\delta(^{119}Sn)$ of the substituted tributyltin(IV) phenolates in $CDCl_3$ solutions with Taft's constant σ_I

Acknowledgements

The financial assistance of the Grant Agency of the Czech Republic (grant No. 203/97/0502) is gratefully acknowledged.

References

1. Davies A.G., Smith P.J.: Chapter 11 - Tin in: G.Wilkinson (Ed.): *Comprehensive Organometallic Chemistry*, p. 519, Pergamon Press, Oxford 1982.
2. Keil B., Herout V., Hudlický M., Ernest I., Protiva M., Gut J., Komers R., Morávek J.: *Laboratorní technika organické chemie*, p. 725, NČSAV, Prague 1963.
3. Dub M.: *Organometallic Compounds* (R.W. Weiss, Ed.), Vol.II. 2nd Edition, p. 361, Springer Verlag 1967.
4. Hilldebrand W.F., Lundell G.E.F., Bright H.A., Hoffman J.I.: *Vybrané methody anorganické analýzy*. SNTL, Prague 1958.

5. Matsuda S., Matsuda H.: Japan. 10,129 (1970). Chem. Abstr. **73**, 45601 (1970).
6. Bloodworth A.J., Davies A.G.: J. Chem. Soc. **1965**, 5238.
7. Khoo L.E., Lee H.H.: Tetrahedron **26**, 4261 (1970).
8. Jacobi E., Lust S., Zima O., van Schoor A.: Ger. 1,045,716 (1958). Chem. Abstr. **54**, 25546 (1960).
9. Pisjelman J., Pereyre M.: J. Organomet. Chem. **44**, 309 (1972).
10. Saruto K., Suenobu Y.: Japan. 6172('66) (1961). Chem. Abstr. **65**, 5490 (1966).
11. Nishimoto I., Fuse G.: Zinn Verwendung **70**, 3 (1966).
12. Nádvorník M., Holeček J., Handlíř K., Lyčka A.: J. Organomet. Chem. **275**, 275 (1984).
13. Holeček J., Lyčka A.: Inorg. Chim. Acta **118**, L15 (1986).
14. Hollein M., Handlíř K.: Sci. Pap. Univ. Pardubice Ser. A **2**, 25 (1996).
15. Kortům G., Vogel W., Andrussov K.: *Dissociacionskonstanten organischer Säuren in wässerigen Lösungen.* Butterworths, London 1961.
16. Exner O.: *Korelační vztahy v organické chemii*, SNTL, Prague 1981.
17. Kuhn R., Wassermann A.: Helv. Chim. Acta **11**, 23 (1928).
18. Bordwell F.G., Boutan P.J.: J. Am. Chem. Soc. **78**, 854 (1956).
19. Wahbi A.M., El-Yazbi F.A., Hewala I.I., Awad A.A.: Pharmacie **48**, 422 (1993).
20. Krahl M.E., Clowes G.H.A.: J. Cellular. Compar. Physiol. **11**, 1 (1938).
21. Ogston A.G.: J. Chem. Soc. **1936**, 1713.
22. Sager E.E., Schooley M.R., Carr A.S., Acree S.F.: J. Res. Natl. Bur. Stand. (U.S.) **35**, 521 (1945).