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Studies in aryltin chemistry. X [1]. Synthesis and NMR spectra (^{119}Sn and ^{13}C) of some *meta*- and *ortho*-substituted tetra- and triaryltin compounds. The crystal and molecular structures of tris(*m*-tolyl)- and tris(3,5-dimethylphenyl)tin(IV) chloride

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Abstract

Several new tetra-aryltin compounds, Ar_4Sn [Ar = 3,5-$(CH_3)_2C_6H_3$, 3,5-$Z_2C_6H_3$, and *m*-ZC_6H_4 (Z = F, Cl)] and Ar_3SnX [X = Cl, Br, I: Ar = 3,5-$(CH_3)_2C_6H_3$, *m*- and *o*-$CH_3OC_6H_4$; X = Br; Ar = *m*-ZC_6H_4 (Z = F, Cl)] have been synthesized by literature methods and complete solution NMR data (^{119}Sn, ^{13}C) are reported for these and other *meta*- and *ortho*-substituted aryltins. *Meta*-substituents appear to exert electronic effects on chemical shifts and coupling constants, but for *ortho*-substituents steric effects appear to predominate. Crystal data show that *meta*-substituted Ar_3SnX have trigonal unit cells in contrast to the monoclinic unit cells adopted by *para*- and *ortho*-substituted Ar_3SnX. Complete crystal structures are reported for (*m*-$CH_3C_6H_4)_3SnCl$: *R*3, *a* = 14.9262(15), *c* = 7.3482(12) Å, *Z* = 3 and (3,5-$(CH_3)_2C_6H_3)_3SnCl$: *R*3*c*, *a* = 15.779(8), *c* = 15.593(4) Å, *Z* = 6. In both cases, all molecules have trigonal symmetry, the first such examples to be reported.

Keywords: Aryltin compounds; Substituent effects; NMR spectra; Crystal structures

1. Introduction

In earlier papers in this series, we have considered the effects of *para*-substituents on the vibrational [2] and NMR (^{119}Sn, ^{13}C) [3] spectra, as well as on the crystal and molecular structures of tetra- and triaryltin compounds [4,5]. The focus of these studies has now shifted to assessing the corresponding effects of *meta*- and *ortho*-substituents, including those due to both substituent type and position [1].

Thus, following on our previous work [3] on *para*-substituent effects in the tin-119 and carbon-13 NMR spectra of various Ar_4Sn and Ar_3SnX (Ar = *p*-ZC_6H_4; X = Cl, Br, I), we now extend these studies to *meta*- and *ortho*-substituted analogues of the above compounds and compare our results with those obtained earlier for the $ArSn(CH_3)_3$ system [6].

In addition, while routine examination showed several Ar_4Sn to have the expected tetragonal space groups [4] and (*o*-$ZC_6H_4)_3SnX$ (Z = CH_3, CH_3O; X = Cl, Br) to be monoclinic like the corresponding Ph_3SnX [7], *meta*-substituted Ar_3SnX unexpectedly crystallise in more symmetric trigonal space groups. This prompted the two full structure determinations reported here.

2. Experimental details

All experimental procedures including microanalyses and solution ($CDCl_3$) NMR spectra measurements were as described earlier [3,8]. Arylmercury(II) bromides prepared by the Grignard method using ether or tetrahydrofuran (THF) [9] were *m*-chlorophenylmercury(II) bromide: yield 50%; m.p. 221 °C (acetone). Anal. Found: C, 18.37; H, 0.96. $C_6H_4BrClHg$ Calc.: C, 18.38; H, 1.03% and the fluoro analogue: m.p. 239 °C (lit. 241–242 °C [10]). Mercuration of mesitylene [11,12] gave mesitylmercury(II) bromide (mesityl = 2,4,6-trimethylphenyl); m.p. 192–193 °C (lit. 194 °C [13]).

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The following aryltins have already been reported: Ar_4Sn. Ar = *m*- or *o*-$CH_3OC_6H_4$ [1]; $(Mes)_3SnX$, Mes = 2,4,6-$(CH_3)_3C_6H_2$; X = Br, I [14].

2.1. Syntheses

All compounds used in this study were prepared by conventional methods, including those newly synthesised which are listed in Table 1.

2.1.1. Method (A)

The Grignard procedure [8]; also used to prepare $(m\text{-Tol})_3Sn$, m.p. 128 °C (lit. 127.5–128.5 °C [15]), $(o\text{-Tol})_3Sn$, m.p. 216 °C (lit. 217.5–219.5 °C [9]) (Tol = $CH_3C_6H_4$), $(m\text{-}CF_3C_6H_4)_3Sn$, m.p. 142 °C (lit. 143 °C [16]), and $(p\text{-}CF_3C_6H_4)_4Sn$, m.p. 148–149 °C (lit. 150–151 °C [9]).

2.1.2. Methods (B) and (C)

The Kocheskov reaction as used for $(m\text{-Tol})_3SnCl$, m.p. 108 °C (lit. 108 °C [17]). (B) Several Ar_3SnBr were prepared as $(m\text{-}CF_3C_6H_4)_3SnBr$ [9] by refluxing a xylene solution of the ArHgBr (vide supra) with tin powder for one to two days (C).

2.1.3. Methods (D)–(F)

Triaryltin iodides were prepared by reacting the required Ar_4Sn with iodine in refluxing CCl_4 (D), e.g. tris(*m*-tolyl)tin iodide, m.p. 63–64 °C (lit. 52 °C [18]), or by refluxing the Ar_3SnCl with excess sodium iodide in acetone for two to three days (E) [19]. Halide exchange (F) [15] to convert Ar_3SnX to Ar_3SnY through the hydroxide and aqueous HY was used to obtain $(o\text{-Tol})_3SnBr$, m.p. 102–104 °C (lit. 101.4–101.9 °C [9]) and $(o\text{-Tol})_3SnI$, m.p. 119–120 °C (lit. 119 °C [20]) from $(o\text{-Tol})_3SnCl$, m.p. 115–117 °C (lit. 115.0–115.7 °C [9]) which was prepared by the literature procedure as was $(m\text{-Tol})_3SnBr$, m.p. 106 °C (lit. 104–105 °C [15]).

2.2. X-ray diffraction studies

Crystals suitable for X-ray investigation were obtained by slow recrystallization from ethanol and X-ray data were collected on an Enraf–Nonius CAD-4 diffractometer. Cell parameters were derived from 25 reflections. A Laue symmetry check as well as a systematic absence verification was used to determine the space group. Complete crystal data sets were obtained for (a) Ar_4Sn (Ar = 3,5-$F_2C_6H_3$, *m*-$CF_3C_6H_4$, *p*-$CF_3C_6H_4$);

Table 1
Analytical data [a]

Ar [b]	Method [c]	Solvent [d]	M.p. (°C)	C (%)	H (%)
Ar_4Sn					
3,5-Xyl	(A) [e]	ethanol	153–155	71.38 (71.26)	6.75 (6.72)
m-ClC_6H_4	(A)	acetone/ethanol	197–198	50.63 (51.06)	3.04 (2.86)
3,5-$Cl_2C_6H_3$	(A)	acetone	161	41.25 (41.02)	1.86 (1.72)
m-FC_6H_4	(A) [e]	acetone	186	57.82 (57.76)	3.48 (3.23)
3,5-$F_2C_6H_3$	(A)	acetone	201–202	49.82 (50.48)	2.26 (2.12)
Ar_3SnCl					
3,5-Xyl	(B)	ethanol	150–151	61.68 (61.38)	5.91 (5.80)
m-Anis	(B)	ethanol	102–103	52.88 (53.04)	4.66 (4.45)
o-Anis	(F) [f]	ethanol	160–162	52.98 (53.04)	4.24 (4.45)
Mes	(F) [g]	acetone	169–171	63.38 (63.38)	6.62 (6.50)
Ar_3SnBr					
3,5-Xyl	(B)	ethanol	163–164	55.86 (56.07)	5.40 (5.29)
m-Anis	(B)	ethanol	90–92	48.02 (48.51)	4.16 (4.07)
o-Anis	(F) [f]	ethanol	168–170	48.86 (48.51)	3.55 (4.07)
m-ClC_6H_4	(C)	ethanol	67–69	39.60 (40.54)	2.06 (2.27)
m-FC_6H_4	(C)	—	< 20	44.52 (44.68)	2.52 (2.50)
Ar_3SnI					
3,5-Xyl	(D)	ethanol	147	51.32 (51.40)	4.72 (4.85)
m-Anis	(E)	ethanol	67-69	42.10 (44.49)	4.10 (3.73)
o-Anis	(D) [h]	ethanol	160	44.17 (44.49)	3.88 (3.73)

[a] Calculated values in parentheses.
[b] Ar: 3,5-Xyl ≡ 3,5-$(CH_3)_2C_6H_3$; *m*-Anis ≡ *m*-$CH_3OC_6H_4$; *o*-Anis ≡ *o*-$CH_3OC_6H_4$; Mes ≡ 2,4,6-$(CH_3)_3C_6H_2$.
[c] See text.
[d] Recrystallisation solvent.
[e] Grignard reagent in THF.
[f] X = I, Y = Cl or Br.
[g] X = Br, Y = Cl.
[h] Reaction in toluene.

Table 2
Crystallographic data and structure determination details

	$(m\text{-}CH_3C_6H_4)_3SnCl$	$(3,5\text{-}(CH_3)_2C_6H_3)_3SnCl$
Crystal data (Mo Kα; λ = 0.70930 Å)		
Molecular formula (*M*)	$C_{21}H_{21}ClSn$ (427.52)	$C_{24}H_{27}ClSn$ (469.62)
Symmetry (space group)	Trigonal (*R*3)	Trigonal (*R*3*c*)
Lattice constants (Å)	$a = 14.9262(15)$, $c = 7.3482(12)$	$a = 15.779(8)$, $c = 15.593(4)$
Cell volume (Å^3); Z	1417.8(3); 3	3362(2); 6
D_c (g cm^{-3})	1.502	1.392
T (K)	290	220
θ-Range (μ (mm^{-1}))	20–22° (1.50)	20–22° (1.27)
Data collection		
Crystal size (mm^3)	0.25{120, 120} × 0.35{011, 011} × 0.39{100, 100}	0.19{110, 110} × 0.25{120, 120} × 0.37{001, 001}
Scan type, θ_{max}, $\Delta\omega = (1.00 + 0.35 \tan\theta)°$	$\omega/2\theta$, 25.0°	ω, 25.0°
h, *k*, *l* ranges	$-14 \rightarrow 15$, $0 \rightarrow 17$, $0 \rightarrow 8$	$0 \rightarrow 16$, $0 \rightarrow 16$, $0 \rightarrow 18$
No. of standard reflections (h^{-1}), intensity variations (%)	7, ±1.0	7, ±2.2
Measured reflections	3340	6630
Independent reflections (R_{int})	1116 (0.020)	1199 (0.030)
Observed reflections, $I \geq 3\sigma(I)$	1116	919
Structure solution and refinement		
No. of parameters, reflections	99, 558	115, 669
R, R_w [a], *S*	0.009, 0.011, 1.15	0.015, 0.018, 1.44
$(\Delta/\sigma)_{max}$	0.35	0.38
$(\Delta\rho)_{min}$, $(\Delta\rho)_{max}$ (e Å^{-3})	−0.26, 0.12	−0.18, 0.49
Secondary extinction	Refined, 0.193(8)	Not refined
Final ΔF map (e Å^{-3})		
General background	≤ 0.12	≤ 0.15
Highest peaks (distances (Å)) atom	none	0.40, 0.38(1.0, 1.1)Sn, 0.18(0.9)Cl
Bijvoet test, hand probability level	0.8×10^{-15}	1.1×10^{-12}

[a] $w^{-1} = \sigma^2(F_o) + 0.0001(F_o)^2$.

(b) Ar_3SnX (X = Cl, Br; Ar = *m*- and *o*-ZC_6H_4 (Z = CH_3, CH_3O)).

For the structure determinations, data collection parameters for tris(*m*-tolyl)tin chloride (**I**) and tris(3,5-dimethylphenyl)tin chloride (**II**) are reported in Table 2. Intensity data were corrected for Lorentz and polarisation effects, but not for absorption. Structure calculations were performed using NRCVAX software [21]. Structure **I** was solved by direct methods (SHELXS-86) [22] and structure **II** by the heavy atom method, then both completed using difference Fourier syntheses. For both compounds, the molecules were located on three-fold axes, so the asymmetric unit was composed of tin, chlorine and only one substituted phenyl ring. Full-matrix least-squares refinement phased on *F* gave the refinement parameters in Table 2, with anisotropic thermal parameters applied for non-hydrogen atoms. Hydrogen atoms were refined isotropically, initially placed in calculated positions, the rotation of the methyl groups obtained from at least one peak of a difference Fourier map and then all hydrogen atoms refined in the final cycles. Anomalous dispersion terms were included for Sn and Cl atoms [23]. While scattering factors were

Table 3
Atom coordinates and equivalent isotropic temperature factors

Atom	*x*	*y*	*z*	B_{iso}
(m-CH$_3$C$_6$H$_4$)$_3$SnCl				
Sn	0	0	0	2.425(4)
Cl	0	0	−0.3238(1)	4.02(3)
C(1)	0.0862(2)	0.1589(2)	0.0719(3)	2.63(9)
C(2)	0.0732(2)	0.1905(2)	0.2433(3)	3.02(9)
C(3)	0.1312(2)	0.2933(2)	0.2972(3)	3.43(10)
C(4)	0.2018(2)	0.3641(2)	0.1760(4)	3.71(11)
C(5)	0.2149(2)	0.3347(2)	0.0049(4)	4.02(11)
C(6)	0.1575(2)	0.2315(2)	−0.0473(3)	3.32(10)
C(31)	0.1160(3)	0.3265(3)	0.4841(4)	5.25(16)
(3,5-(CH$_3$)$_2$C$_6$H$_3$)$_3$SnCl				
Sn	0	0	0	3.376(10)
Cl	0	0	−0.1512(1)	4.59(6)
C(1)	0.0724(3)	−0.0763(3)	0.0397(3)	3.7(2)
C(2)	0.0530(4)	−0.1175(3)	0.1214(3)	4.4(2)
C(3)	0.1045(4)	−0.1605(4)	0.1540(3)	5.1(3)
C(4)	0.1762(4)	−0.1610(4)	0.1025(4)	5.0(3)
C(5)	0.1955(4)	−0.1230(4)	0.0218(3)	4.8(3)
C(6)	0.1425(3)	−0.0807(3)	−0.0100(3)	3.9(2)
C(31)	0.0861(6)	−0.2012(6)	0.2432(4)	7.7(5)
C(51)	0.2745(5)	−0.1243 (5)	−0.0316(4)	7.3(5)

B_{iso} is the mean of the principal axes of the thermal ellipsoid.

from the literature [24], the enantiomorphy was confirmed by Bijvoet analysis of the Friedel pair reflections. Final atom coordinates (non-hydrogen atoms) and isotropic thermal parameters are given in Table 3. Tables of crystal data sets, anisotropic thermal parameters, complete bond lengths and angles, and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre. Structure factor lists are available from M.G.S.

3. Results and discussion

3.1. NMR studies

3.1.1. Tin-119 data

Tin-119 chemical shifts for all compounds examined in this work are given in Table 4. The trend in $(m\text{-}YC_6H_4)_4Sn$ values clearly parallels that for the *para*-compounds (Fig. 1), as was found earlier for the

Table 4
^{119}Sn NMR data for Ar_4Sn and Ar_3SnX in $CDCl_3$

No.	Ar [a]	Conc. (M)	$\delta(^{119}Sn)$ (ppm)	$^nJ(^{119}Sn-^{13}C)$ (Hz) [b]					
				$n=1$	$n=2$ [c]	$n=2$	$n=3$ [c]	$n=3$	$n=4$
Ar_4Sn									
(A)	C_6H_5 [d]	sat.	−128.84	531.1	35.5	—	53.1	—	10.7
(1)	*m*-Tol	0.274	−128.01	527.4	36.2	36.7	50.3	53.5	11.3
(2)	3,5-Xyl	0.224	−127.50	521.8	36.3	—	53.0	—	11.4
(3)	*m*-Anis	0.334	−125.13	529.0	42.0	34.8	64.7	60.1	10.6
(4)	*o*-Tol	sat.	−122.61	520.8	32.1	41.2	42.4	51.7	10.1
(5)	*o*-Anis	0.093	−136.30	575.8	n.o.	31.1	27.7	54.7	n.o.
(6)	*m*-ClC_6H_4	0.286	−126.32	532.0	41.8	35.3	69.9	56.6	10.8
(7)	3,5-$Cl_2C_6H_3$	0.189	−122.65	535.0	40.5	—	76.9	—	9.7
(8)	*m*-FC_6H_4	0.092	−126.66	537.3	41.4	34.8	73.4	61.2	10.2
(9)	3,5-$F_2C_6H_3$	sat.	−119.58	544.2	40.6	—	89.8	—	
(10)	*p*-$CF_3C_6H_4$	0.183	−134.02	536.8	40.1	—	53.1	—	12.2
(11)	*m*-$CF_3C_6H_4$	sat.	−126.31	n.o.	43.8	40.0	n.o.	52.8	n.o.
Ar_3SnCl									
(B)	C_6H_5 [d]	0.261	−44.81	615.7	49.8	—	63.5	—	13.2
(12)	*m*-Tol	0.291	−42.33	607.6	49.3	47.7	62.9	66.5	14.0
(13)	3,5-Xyl	0.217	−39.68	602.6	48.5	—	65.5	—	13.7
(14)	*m*-Anis	0.411	−44.02	615.2	54.0	48.3	78.6	76.1	13.0
(15)	*o*-Tol	0.193	−32.28	603.9	42.1	53.5	53.8	64.9	12.0
(16)	Mes	0.215	−84.39	596.1	45.2	—	54.2	—	11.3
(17)	*o*-Anis	0.260	−56.68	684.8	n.o.	34.1	35.2	67.6	9.4
Ar_3SnBr									
(C)	C_6H_5 [d]	0.236	−60.01	596.3	49.4	—	62.5	—	14.9
(18)	*m*-Tol	0.271	−56.87	590.5	49.3	47.4	61.8	65.9	13.6
(19)	3,5-Xyl	0.238	−53.55	584.4	48.5	—	66.9	—	13.7
(20)	*m*-Anis	0.250	−58.51	596.1	54.4	48.0	81.6	74.6	12.8
(21)	*o*-Tol	0.235	−53.98	586.1	41.9	54.2	53.0	64.2	11.8
(22)	Mes	0.197	−120.98	579.8	45.3	—	53.6	—	11.2
(23)	*o*-Anis	0.201	−74.31	666.2	9.4	35.3	34.5	67.8	8.8
(24)	*m*-ClC_6H_4	0.285	−67.58	599.4	54.2	47.0	84.0	71.4	12.5
(25)	*m*-FC_6H_4	0.439	−67.31	608.8	53.8	46.7	88.6	75.3	12.3
(26)	*m*-$CF_3C_6H_4$	0.346	−67.80	613.9	56.6	49.2	n.o.	64.1	n.o.
Ar_3SnI									
(D)	C_6H_5 [d]	0.249	−113.38	570.9	48.6	—	61.1	—	14.6
(27)	*m*-Tol	0.325	−108.47	563.6	48.4	47.4	61.8	65.9	13.6
(28)	3,5-Xyl	0.209	−103.71	558.8	47.7	—	64.7	—	13.8
(29)	*m*-Anis	0.206	−110.52	568.1	54.0	47.3	78.2	73.6	12.3
(30)	*o*-Tol	0.161	−121.84	559.4	40.9	53.7	51.6	64.0	12.6
(31)	Mes	0.298	−217.10	554.0	43.7	—	52.5	—	11.8
(32)	*o*-Anis	0.398	−135.65	635.8	n.o.	34.1	33.1	67.6	9.4

[a] Tol = $CH_3C_6H_4$, Xyl = $(CH_3)_2C_6H_3$, Anis = $CH_3OC_6H_4$, Mes = 2,4,6-$(CH_3)_3C_6H_2$.
[b] Data from carbon-13 spectra.
[c] On substituent side of phenyl ring.
[d] [3].

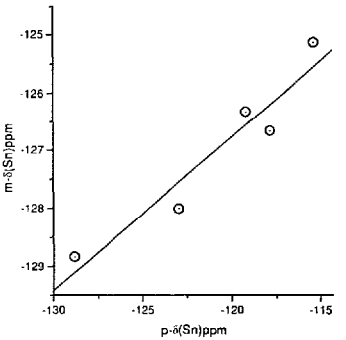

Fig. 1. Tin-119 chemical shifts: values for $(p\text{-}YC_6H_4)_3Sn$ plotted against those for $(m\text{-}YC_6H_4)_3Sn$.

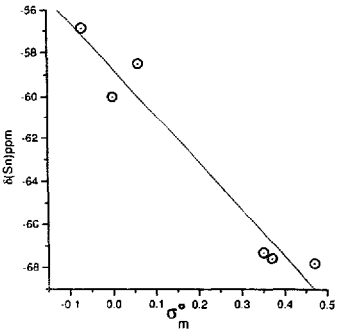

Fig. 3. Tin-119 chemical shifts for $(m\text{-}YC_6H_4)SnBr$ plotted against σ_m°.

$ArSn(CH_3)_3$ system [6], but in contrast to that case, for Ar_4Sn the overall $\delta(^{119}Sn)$ range is less for the *meta*-compounds than in the *para*-series. Both Ar_4Sn series show the same dependence on the resonance parameter [25] σ_R or σ_R° (Fig. 2), the point for tetraphenyltin being included in both cases. These results are consistent with the earlier suggestion [3] that for Ar_4Sn the substituent effect depends on the π-electron donor ability of the substituents (signified by σ_R or σ_R° values) to increase π-electron density at the *ipso*-carbon and thus indirectly cause a shift of the ^{119}Sn resonance to higher frequency.

In agreement with this picture, the *meta*-effect on $\delta(^{119}Sn)$ is less than the *para*-effect but is synergic, the effect increasing as $F > Cl > CH_3$, i.e. as the substituents are better π-donors. In contrast, the substituent

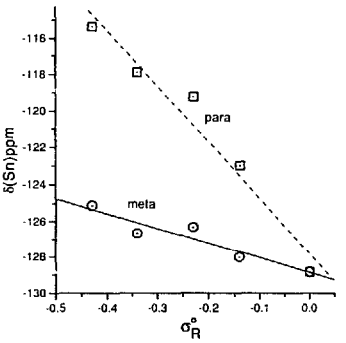

Fig. 2. Tin-119 chemical shifts for $(p\text{-}Y_6H_4)_4Sn$ (□) or $(m\text{-}YC_6H_4)_4Sn$ (○) plotted against σ_R°.

effect of the weak π-acceptor group, CF_3 ($\sigma_R^\circ = 0.10$ [25]) does not follow from the trends shown in Fig. 2, $\delta(^{119}Sn)$ being at lower (*para*) or higher (*meta*) frequency than the predicted values, −130.9 and −129.7 ppm respectively. This implies that a different substituent effect mechanism is required for this case. Lastly, we note, as for the $ArSn(CH_3)_3$ system [6], that tin-119 shifts for Ar_4Sn correlate well with shifts of lead-207 in the corresponding Ar_4Pb compounds [26]. Thus the overall correlation has $\delta(^{207}Pb) = 2.06\delta(^{119}Sn) + 88.3$ ($n = 11$, $r = 0.984$), which is consistent with the more general one noted for ^{207}Pb and ^{119}Sn chemical shifts [27] as well as that for a limited number of tetra-aryls [28]. Our data permit analysis by substituent position, *para*: $\delta(^{207}Pb) = 1.99\delta(^{119}Sn) + 78.6$ ($n = 5$, $r = 0.996$), *meta*: $\delta(^{207}Pb) = 3.19\delta(^{119}Sn) + 232.5$ ($n = 5$, $r = 0.995$), *ortho*: $\delta(^{207}Pb) = 2.48\delta(^{119}Sn) + 141.7$ ($n = 3$, $r = 0.999$). This would indicate that while substituent effects in Ar_4Sn and Ar_4Pb are very similar, they are not identical.

Only the Ar_3SnBr series was studied in the same detail as the Ar_4Sn system. Comparison of $\delta(^{119}Sn)$ values for the *para*- and *meta*-analogues shows no correlation ($r = 0.42$), but the chemical shifts for the *meta*-series do correlate well with σ_m or better σ_m° (Fig. 3), even with the datum point for the CF_3 substituent included. This would imply that for $(m\text{-}YC_6H_4)_3SnBr$ a ground state substituent effect predominates, that is, as Y becomes more electron attracting overall, the ionic character of the Sn–Br bond diminishes and the tin resonance shifts to lower frequency [29].

Two distinct *ortho*-effects are observed using CH_3 and CH_3O as substituents. For *o*-CH_3 in Ar_4Sn and Ar_3SnX (X = Cl, Br), an increase in frequency for $\delta(^{119}Sn)$, almost the same as for *p*-CH_3, is seen. This is

probably an electronic effect since σ_o° [25] has almost the same value as (σ_p, σ_p°) and (σ_R, σ_R°) for this substituent. However, for (*o*-Tol)$_3$SnI a decrease in $\delta(^{119}Sn)$ occurs. This effect is magnified with CH_3O as the *ortho*-group and changes for Ar_3SnX as X = Ar < Cl < Br < I. The effect of two *o*-CH_3 groups in the (Mes)$_3$SnX series is even more dramatic, with δ^{119}_{Sn} = −217.10 ppm for (Mes)$_3$SnI approaching the range appropriate to five-coordinate triphenyltin halide systems [30].

Table 5
^{13}C NMR chemical shifts (ppm) for Ar_4Sn and Ar_3SnX in $CDCl_3$

No. [a]	*i*-C	*o*-C [b]	*o*-C	*m*-C [b]	*m*-C	*p*-C	
Ar_4Sn							
(A)	138.04	137.31		128.69		129.17	
(1)	137.95	134.26	137.77	137.95	128.33	129.84	*CH_3*: $\delta(^{13}C)$ 21.53; $^4J(^{119}Sn-^{13}C)$ 4.0
(2)	138.09	134.95	—	137.66	—	130.78	*CH_3*: $\delta(^{13}C)$ 21.41
(3)	138.86	122.55	129.33	159.40	129.50	114.34	*CH_3O*: $\delta(^{13}C)$ 55.00
(4)	139.64	145.00	137.42	129.59	125.77	129.14	*CH_3*: $\delta(^{13}C)$ 25.05; $^3J(^{119}Sn-^{13}C)$ 27.6
(5)	130.12	163.57	138.00	109.50	121.04	129.66	*CH_3O*: $\delta(^{13}C)$ 55.14
(6)	138.28	136.29	134.82	135.42	130.24	130.00	
(7)	138.04	134.17	—	136.38	—	130.72	
(8)	138.61	123.25	132.54	162.99	130.50	116.80	$^1J(^{19}F-m^{13}C)$ 251.5, $^2J(^{19}F-p^{13}C)$ 21.1, $^2J(^{19}F-o^{13}C)$ 18.8, $^3J(^{19}F-m^{13}C)$ 6.7, $^1J(^{19}F-i^{13}C)$ 3.3, $^4J(^{19}F-o^{13}C)$ 3.2, $^4J(^{119}Sn-^{19}F)$ 28.2 [c]
(9)	138.31	118.98	—	163.47	—	106.12	$^1J(^{19}F-m^{13}C)$ 256.4, $^2J(^{19}F-p^{13}C)$ 24.7, $^2J(^{19}F-c^{13}C)$ 15.7, $^3J(^{19}F-m^{13}C)$ 10.2, $^3J(^{19}F-i^{13}C)$ 4.6, $^4J(^{19}F-o^{13}C)$ 6.9, $^4J(^{119}Sn-^{19}F)$ 31.8 [c]
(10)	140.79	137.30	—	125.57	—	132.17	*CF_3*: $\delta(^{13}C)$ 123.94; $^1J(^{19}F-^{13}C)$ 272.4, $^2J(^{19}F-p^{13}C)$ 32.5, $^3J(^{19}F-m^{13}C)$ 3.6, $^5J(^{19}F-i^{13}C)$ 5.2
(11)	136.84	133.13	140.26	131.41	129.42	126.89	*CF_3*: $\delta(^{13}C)$ 124.02; $^1J(^{19}F-^{13}C)$ 272.9, $^2J(^{19}F-m^{13}C)$ 32.1, $^3J(^{19}F-o^{13}C)$ 3.8, $^3J(^{19}F-p^{13}C)$ 3.8, $^4J(^{19}F-m^{13}C)$ 1.4
Ar_3SnCl							
(B)	137.39	136.18		129.03		130.24	
(12)	137.21	133.06	136.57	138.74	128.84	131.20	*CH_3*: $\delta(^{13}C)$ 21.49; $^4J(^{119}Sn-^{13}C)$ 4.6
(13)	137.15	133.34	—	138.44	—	132.11	*CH_3*: $\delta(^{13}C)$ 21.36; $^4J(^{119}Sn-^{13}C)$ 5.4
(14)	138.06	121.20	128.05	159.76	130.00	115.95	*CH_3O*: $\delta(^{13}C)$ 55.15
(15)	138.69	144.55	136.27	130.13	126.10	130.49	*CH_3*: $\delta(^{13}C)$ 24.69; $^3J(^{119}Sn-^{13}C)$ 35.3
(16)	141.37	144.10	—	128.98	—	139.50	*o-CH_3*: $\delta(^{13}C)$ 25.21; $^3J(^{119}Sn-^{13}C)$ 40.4, *p-CH_3*: $\delta(^{13}C)$ 21.01
(17)	129.13	162.76	136.54	109.99	121.73	131.32	*CH_3O*: $\delta(^{13}C)$ 55.47
Ar_3SnBr							
(C)	137.16	136.37	—	129.32	—	130.58	
(18)	136.87	133.12	136.65	138.70	128.80	131.13	*CH_3*: $\delta(^{13}C)$ 21.50
(19)	136.82	133.64	—	138.38	—	132.04	*CH_3*: $\delta(^{13}C)$ 21.35; $^4J(^{119}Sn-^{13}C)$ 5.4
(20)	137.78	121.33	128.14	159.72	129.95	115.87	*CH_3O*: $\delta(^{13}C)$ 55.19
(21)	138.12	144.53	136.46	130.17	126.11	130.48	*CH_3*: $\delta(^{13}C)$ 24.77; $^3J(^{119}Sn-^{13}C)$ 34.7
(22)	141.14	144.18	—	129.12	—	139.54	*o-CH_3*: $\delta(^{13}C)$ 25.71; $^3J(^{119}Sn-^{13}C)$ 40.6, *p-CH_3*: $\delta(^{13}C)$ 21.11
(23)	128.82	162.71	136.77	110.02	121.71	131.33	*CH_3O*: $\delta(^{13}C)$ 55.46
(24)	137.71	135.45	133.85	135.72	130.49	130.98	
(25)	137.94	122.53	131.60	163.00	130.84	117.89	$^1J(^{19}F-m^{13}C)$ 252.5, $^2J(^{19}F-p^{13}C)$ 20.8, $^2J(^{19}F-o^{13}C)$ 19.7, $^3J(^{19}F-m^{13}C)$ 7.1, $^3J(^{19}F-i^{13}C)$ 3.8, $^4J(^{19}F-o^{13}C)$ 3.2, $^4J(^{119}Sn-^{19}F)$ 34.4 [c]
Ar_3SnI							
(26)	136.67	132.39	139.36	131.72	129.72	127.78	*CF_3*: $\delta(^{13}C)$ 123.85; $^1J(^{19}F-^{13}C)$ 272.8, $^2J(^{19}F-m^{13}C)$ 32.4, $^3J(^{19}F-o^{13}C)$ 3.6, $^3J(^{19}F-p^{13}C)$ 3.6
(D)	136.30	136.30	—	129.03	—	130.24	
(27)	136.24	133.25	136.79	138.60	128.72	130.99	*CH_3*: $\delta(^{13}C)$ 21.51
(28)	136.19	133.78	—	138.27	—	131.90	*CH_3*: $\delta(^{13}C)$ 21.35; $^4J(^{119}Sn-^{13}C)$ 5.3
(29)	137.17	121.58	128.25	159.62	129.85	115.69	*CH_3O*: $\delta(^{13}C)$ 55.21
(30)	136.94	144.44	136.81	130.20	126.07	130.42	*CH_3*: $\delta(^{13}C)$ 24.94; $^3J(^{119}Sn-^{13}C)$ 34.8
(31)	140.14	144.02	—	129.00	—	139.30	*o-CH_3*: $\delta(^{13}C)$ 26.27; $^3J(^{119}Sn-^{13}C)$ 40.7, *p-CH_3*: $\delta(^{13}C)$ 20.96
(32)	127.94	162.59	137.03	110.04	121.54	131.29	*CH_3O*: $\delta(^{13}C)$ 55.35

[a] See Table 4.
[b] On substituent side of phenyl ring.
[c] Data from tin-119 spectra.

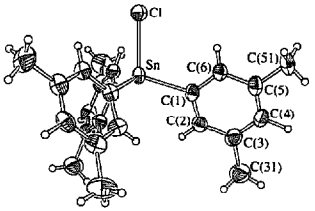

Fig. 4. View of the molecule (3,5-$(CH_3)_2C_6H_3)_3SnCl$ (II) showing the numbering scheme for I and II.

Table 6
Selected bond lengths (Å) and angles (°)

(a) (m-$CH_3C_6H_4)_3SnCl$			
Sn—Cl	2.379(1)	Cl···Sn [a]	4.969(1)
Sn–C(1)	2.124(2)	C(3)–C(31)	1.515(4)
C(1)–C(2)	1.392(3)	C(1)–C(6)	1.386(3)
Cl–Sn–C(1)	104.40(6)	C(1)–Sn–C(1) [b]	114.03(14)
Sn–C(1)–C(2)	119.61(15)	Sn–C(1)–C(6)	121.02(16)
Cl–Sn–C(1)–C(2)	158.2(1)	Cl–Sn–C(1)–C(6)	−23.7(1)
(b) (3,5-$(CH_3)_2C_6H_3)_3SnCl$			
Sn—Cl	2.3575(2)	Cl···Sn [c]	5.439(2)
Sn–C(1)	2.124(4)	C(3)–C(31)	1.498(8)
C(5)–C(51)	1.509(8)	C(1)–C(2)	1.393(6)
C(1)–C(6)	1.381(6)		
Cl–Sn–C(1)	106.965(1)	C(1)–Sn–C(1) [b]	111.9(2)
Sn–C(1)–C(2)	118.4(3)	Sn–C(1)–C(6)	122.4(3)
Cl–Sn–C(1)–C(2)	−157.2(3)	Cl–Sn–C(1)–C(6)	27.3(2)

[a] 0.0,1 + z.
[b] y,x − y,z or y − x,x,z.
[c] 0.0,z + 1/2.

3.1.2. Carbon-13 data

One bond ($^{119}Sn-^{13}C$) coupling constants (Table 4) for Ar_3Sn and Ar_3SnBr (Ar = *m*-YC_6H_4) both qualitatively correlate with σ_I, σ_m, or σ_m° ($n = 5$ (with CF_3); $r = 0.74–0.78$ (Ar_4Sn), $r = 0.82–0.81$ (Ar_3SnBr)) which is in contrast with the inverse quantitative correlation with σ_R or σ_R° found for *para*-substituents [3]. Thus, the electronic effects are opposite, *meta*-substituents which are better σ-electron acceptors cause $^1J_{Sn-C}$ values to increase while *para*-substituents must be stronger π-electron donors to have the same effect. The effects of CH_3 and CH_3O as *ortho*-substituents are contradictory, as shown by the orders of $^1J_{Sn-C}$ data, for all four aryltin systems examined: CH_3, $o < m < p$, but for CH_3O, $m < p < o$.

Carbon-13 chemical shift data (Table 5) show changes typical of the corresponding substituted benzenes and can be closely reproduced (±2 ppm) by the additivity rule [31] (A), $\delta(\text{ppm}) = 128.5 + \Sigma Z_\alpha(X)$, where $Z_\alpha(X)$ is the substituent chemical shift parameter (ppm) for the given position (*a*) derived from data for the appropriate C_6H_5X. This has already been validated for various Ar_4M (M = Si–Pb) [32]. Our results (available from the authors (I.W.)) extend this agreement to Ar_3SnX (X = Cl, Br, I), the calculations taking into account the slight variation in $Z_\alpha(Sn)$ required with different aryltin systems [33]. Of more interest are systems which do not agree with (A), i.e. *o*-anisyl- or mesityltin compounds. For both series, the $\delta(^{13}C)$ values for the *ipso*-carbon are approximately 6 ppm to higher frequency than the values calculated using (A), a change noted also for triphenyltin systems ongoing from four- to five-coordination at tin [30].

3.1.3. The ortho-effect

The steric *ortho*-effect seen in this work was also observed earlier for the $ArSn(CH_3)_3$ system [6], and has also been reported in the spectra of triarylphosphines and their derivatives [34–36]. In both $Ar_3P(X)$ and Ar_3SnX cases, the *ortho*-effect varies with the group X. In fact, this *ortho*-effect is a particular example of the more general 'γ-effect' in the spectra of heavy nuclei (i.e. ^{13}C, ^{19}F, ^{31}P, etc.) [37] where, for example, methyl substitution at the γ-position in the fragment $Y_\gamma–X_\beta–Y_\alpha–Z_\beta$ may cause a shift to lower frequency (upfield) of the $\delta(Y)$ value for the nucleus Y_α, and this has been correlated with an increase in the X–Y–Z bond angle [38]. It would thus be of interest to correlate the large

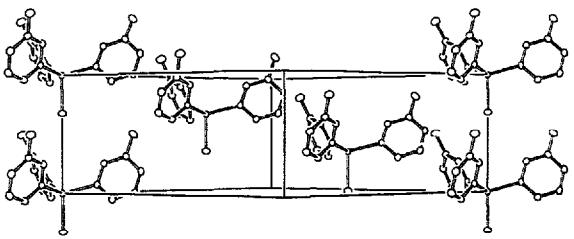

Fig. 5. Packing diagram for (*m*-$CH_3C_6H_4)_3SnCl$ (I); view perpendicular to the *c*-axis.

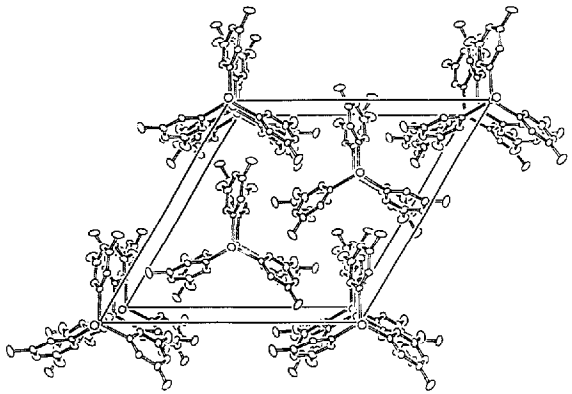

Fig. 6. Packing diagram for II: view down the *c*-axis.

ortho-effect for $(Mes)_3SnI$ compared with Ph_3SnI, with the change in the geometry around tin found in the crystal structures of these compounds [14]. Similarly, the *ortho*-effects of the CH_3O– group seen in the spectra of $(o\text{-Anis})_4Sn$ and $(o\text{-Anis})_3SnX$ (X = Cl, Br, I), which include an increase in the $^1J_{(Sn-C)}$ value, possibly a sign of increased coordination at tin [30], may correlate with the shorter Sn–O distances found in the crystal structures of $(o\text{-Anis})_4Sn$ [1,39] and $(o\text{-Anis})_3SnI$ [40], which might indicate weak Sn–O interactions, increasing the coordination at tin. However, such correlations of *ortho*-effects deduced from solution NMR studies with solid-state structural data must be viewed as completely speculative and clearly solid-state NMR data are required for more definitive conclusions to be drawn.

3.2. Structures of $(m\text{-}CH_3C_6H_4)_3SnCl$ (I) and $(3,5\text{-}(CH_3)_2C_6H_3)_3SnCl$ (II)

Crystal data for both **I** and **II** (Table 2) as well as for $(m\text{-}CH_3OC_6H_4)_3SnX$ (X = Cl, Br) [41] show the compounds to have trigonal space groups which, in fact, correspond to their molecular symmetry, shown for **II** in Fig. 4 with selected geometric parameters in Table 6. In both compounds, the molecules pack closely head to tail (Fig. 5), with the Sn–Cl bonds lying on the three-fold principal axes. Thus, both **I** and **II** have the trigonal propeller conformation required for the lowest molecular energy. In contrast, nearly all other Ar_3SnX structures have unsymmetric molecules which pack in space groups $P2_1/c$ ($P2_1/a$ or $P2_1/n$) or pseudo-$P2_1/c$ ($P\bar{1}$) [7,14,40] which are required to maximize crystal packing efficiency, even though they are not then in the lowest molecular energy conformation [42].

All intermolecular interatomic distances in **I** are greater than van der Waals, the most significant interaction being the approach of a methyl hydrogen to *o*- and *m*-carbon atoms (2.93–2.95 Å) in a phenyl ring of a molecule in a neighbouring column. Simulation of the crystal structure of **II** by replacing *meta*-hydrogens in **I** with methyl groups gives rise to short intercolumn H–H interactions (1.82–1.92 Å). This steric strain is accommodated in the structure of **II** by (a) increasing the intermolecular distance (Sn–Cl) in the chain so the molecules are further apart and (b) the bending of phenyl rings in these molecules away from each other so the orientation of rings of molecules in the same column alternates down the 'chain' (Fig. 6), i.e. both enantiomorph confirmations are present in **II** as compared with one in the case of **I**.

Recently, a trigonal polymorph of triphenyltin chloride has been identified [43]. However, the structure has a trigonal Ph_3SnCl surrounded by three equivalent asymmetric Ph_3SnCl molecules so that the 'tetramer' can still pack efficiently in the resulting crystal. The structures of **I** and **II** are thus the first example of Ar_3SnX structures where all molecules have the trigonal symmetry expected for the lowest molecular energy conformation.

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