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Studies in Aryltin Chemistry.
Part 5. Tin-119 and Carbon-13 NMR Spectra of some Tetra- and Tri-aryltin Compounds*

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Abstract

Tin-119 and carbon-13 NMR data are reported for Ar_4Sn and Ar_3SnX (X = Cl, Br, I) where Ar = p-YC_6H_4 (Y = H, F, Cl, CH_3, CH_3O, CH_3S) as well as $(p\text{-}PhC_6H_4)_4Sn$, all in $CDCl_3$. The ^{119}Sn chemical shifts in all series are unusual in that electron-donating substituents cause shifts to higher frequency (less shielding) from the parent phenyltin compound and two series correlate well with substituent constants, Ar_4Sn (σ_R or σ_R°) and Ar_3SnI (σ_p or σ_p°) if the Y = H points are omitted. All four series show good correlation ($r > 0.95$) with pairs of substituent constants (σ_I, σ_R) or (σ_I, σ_R°); again the Y = H data must be omitted for this to be the case. Tin-119 spectra of $(p\text{-}YC_6H_4)_3SnNCS$ in $CDCl_3$ show $^{119}Sn-^{14}N$ coupling when Y = H, CH_3, and Ph, but not with Y = F or Cl. $^nJ(^{119}Sn-^{13}C)$ values for all four systems correlate well ($r > 0.95$) with the *same* substituent parameters (σ_R or σ_R°) while carbon-13 chemical shifts vary with σ_R in the same way for all four groups of compounds.

Introduction

Studies of electronic substituent effects on NMR chemical shifts date back to the earliest days of NMR spectroscopy and have been reported for a wide range of nuclei [1]. For benzene derivatives where the observed nucleus is *para* or *meta* to the substituent the trends in chemical shift changes may be positive (increased shielding with more electron-donating substituents) or negative (decreased shielding with the same substituents) depending on the chemical system studied. Thus positive trends in chemical shifts were noted for aryl compounds of ^{29}Si, ^{13}C, ^{19}F, ^1H and ^{15}N [2] while aryl compounds of ^{31}P, ^{199}Hg, ^{205}Tl and ^{207}Pb show the reverse effect [3]. However, this chemical shift trend reversal can occur with the same nucleus, thus for p-YC_6H_4-SiX_3, ^{29}Si chemical shifts show a positive correlation with Hammett σ constants for Y = H or CH_3, while the trend is negative with Y = F, Cl or OEt [4], indicating comparisons for different nuclei should be made using analogous chemical systems.

Fewer data are available to demonstrate substituent effects in aryltin compounds. Early, fragmentary results for Ar_4Sn [5] did not show any relation between tin-119 chemical shifts and Hammett constants but a much more detailed study of p-, m- or o-$YC_6H_4SnMe_3$ [6] gave positive trends in ^{119}Sn chemical shifts for all three series, with dual parameter substituent (DSP) analysis showing the polar substituent (σ_I) effect predominating.

The work reported here is part of a study of the effect of benzene ring substitution on the chemical and biological properties of aryltin compounds (Part 4, ref. 7), with the emphasis being on the fungicidal properties of Ar_3SnOH and Ar_3SnOAc systems (Ar ≡ p-YC_6H_4). This has required the preparation of Ar_4Sn and Ar_3SnX (X = Cl, Br, I) as intermediates in the syntheses of these analogues of the triphenyltin compounds presently being used in agriculture [8]. All these intermediate compounds have been fully characterised by several spectroscopic techniques including infrared and Raman spectroscopy [9], mass spectrometry [10], and as reported in this paper tin-119 and carbon-13 NMR spectroscopy. These latter results complement the ^{119}Sn NMR data given earlier [6] and extend the carbon-13 NMR data recently reported for some tri-aryltin compounds [11].

Experimental

Solvents were stored over molecular sieves before use except anhydrous ether (Fisher) used as received while tetrahydrofuran (THF) was distilled from sodium as required. Tin tetrachloride (J. T. Baker) and tetrabromide (Alfa) were used as received as were all p-substituted bromobenzenes (Aldrich) required. Microanalyses for C, H and N were done by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

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Tetra-aryltins were prepared by reacting the appropriate Grignard reagent in ether or THF with tin tetrachloride, for example tetra(p-tolyl)tin, melting point (m.p.) 229–230 °C (lit. [12] 233.5 °C, [13] 232–234 °C) and tetra(p-biphenylyl)tin, m.p. 258–259 °C (lit. [14] 260 °C). Tri-aryltin chlorides and bromides prepared by the Kocheshkov redistribution reaction [15] included tris(p-tolyl)tin chloride, m.p. 96.5–97.0 °C (lit. [12] 97.5 °C) and bromide, m.p. 97–98 °C (lit. [12] 98.5 °C), while treating the chloride with excess sodium iodide in boiling acetone gave tris(p-tolyl)tin iodide, m.p. 118–119 °C (lit. [12] 120.5 °C). Tri-aryltin isothiocyanates were obtained by refluxing a methanol solution of chloride with excess potassium thiocyanate overnight and then adding the methanol filtrate to well stirred ice-cold water. However, tris(p-biphenylyl)tin isothiocyanate was synthesised by Srivastava's method [16] from the iodide (obtained by reacting tetra(p-biphenylyl)tin with iodine in boiling toluene) while tris(p-tolyl)tin isothiocyanate was made by the literature method, m.p. 131 °C (lit. [11] 133–134 °C; [16] 128 °C). Analytical data for new compounds prepared by the above procedures are listed in Table 1 while the other compounds mentioned in this paper are either previous preparations [9, 17] or commercially available.

Nuclear magnetic resonance spectra were recorded on a 300 MHz Varian XL300 FT spectrometer operating at 75.429 (^{13}C), 282.203 (^{19}F) and 111.862 (^{119}Sn) MHz, with digital resolutions of 1.03 (±0.014 ppm), 2.67 (±0.009$_5$ ppm) and 2.27 (±0.020 ppm) Hz respectively. Samples were examined as $CDCl_3$ solutions using as references Me_4Si (internal), $CFCl_3$ (internal), or Me_4Sn (external), the deuterated solvent providing the internal lock. All spectra were measured at room temperature (22 ± 1 °C).

Results

(a) Tin-119 Data

Tin-119 chemical shifts for $(p\text{-}YC_6H_4)_4Sn$ and $(p\text{-}YC_6H_4)_3SnX$ (X = Cl, Br, I, NCS) examined in this work are given in Table 2. In agreement with the previous report [5], $\delta(^{119}Sn)$ values for the tetra-aryltins show no correlation with σ_p or σ_p° constants, but do correlate well with the resonance parameters σ_R or σ_R° (Fig. 1). Unfortunately, straight lines determined using all data points had $r < 0.95$, thus the lines in Fig. 1 were calculated omitting the Ph_4Sn datum point. The same negative chemical shift trend with more electron donating *para*-sub-

TABLE 1. Analytical Data[a]

Compound	Solvent[b]	Melting point (°C)	C (%)	H (%)	N (%)
$(p\text{-}CH_3OC_6H_4)_3SnX$					
X = Cl	hexane	63–64	53.4 (53.0)	4.6 (4.45)	
X = Br	ether/hexane	71–72	48.1 (48.5)	4.1 (4.1)	
X = I	cyclohexane	91–92	44.1 (44.5)	3.7 (3.7)	
$(p\text{-}CH_3SC_6H_4)_3SnX$					
X = Cl	ether	102–103	48.0 (48.2)	4.1 (4.0)	
X = Br	ether	106–107	44.2 (44.4)	3.6 (3.7)	
X = I	acetone/ether	128–129	40.6 (41.0)	3.5 (3.4)	
$(p\text{-}YC_6H_4)_3SnNCS$					
Y = F		160–162	49.15 (49.4)	2.8 (2.6)	2.6 (3.0)
Y = Cl		171–173	44.65 (44.6)	2.2 (2.4)	2.6 (2.7)
Y = Ph	benzene/cyclohexane	202–207d[c]	69.45 (69.8)	4.7 (4.3)	2.25 (2.2)

[a] Calculated values in parentheses. [b] Solvent for recrystallisation. [c] Melts with decomposition.

TABLE 2. ^{119}Sn NMR Parameters of Ar_4Sn and Ar_3SnX ($Ar \equiv p$-YC_6H_4) in $CDCl_3$

No.	Y	Concentration (M)	δ(^{119}Sn) (ppm)	$^nJ(^{119}Sn-^{13}C)$ (Hz)[a] $n = 1$	$n = 2$	$n = 3$	$n = 4$
Ar_4Sn							
1	H	satd.[b]	−128.84	531.1	35.5	53.1	10.7
2	F	0.406	−117.89	551.0	37.8	56.3	14.4
3	Cl	0.273	−119.24	544.2	41.0	56.0	–
4	CH_3	0.110	−122.98	536.6	38.2	52.4	12.7
5	CH_3O	0.272	−115.38	552.5	41.9	55.8	10.2
6	CH_3S	0.279	−119.53	542.7	38.6	51.8	9.0
7	Ph	0.097	−123.89	534.6	38.7	51.9	11.4
Ar_3SnCl							
8	H	0.261	−44.81	615.7	49.8	63.5	13.2
9	F	0.395	−36.61	643.6	57.2	70.6	16.4
10	Cl	0.396	−39.30	634.4	54.4	68.9	16.2
11	CH_3	0.351	−35.91	624.8	51.8	65.5	12.7
12	CH_3O	0.323	−27.36	647.0	56.3	69.9	14.4
13	CH_3S	0.138	−35.49	635.3	54.1	66.8	15.3
Ar_3SnBr							
14	H	0.236	−60.01	596.3	49.4	62.5	14.9
15	F	0.265	−54.39	623.8	59.7	71.6	15.8
16	Cl	0.220	−56.99	614.2	56.1	69.3	16.5
17	CH_3	0.274	−52.17	606.8	50.3	66.0	12.6
18	CH_3O	0.250	−44.89	629.0	56.3	68.5	16.2
19	CH_3S	0.219	−52.44	615.4	54.1	67.3	15.2
Ar_3SnI							
20	H	0.249	−113.38	570.9	48.6	61.1	14.6
21	F	0.448	−113.63	593.2	59.2	71.2	15.6
22	Cl	0.227	−116.46	574.4	55.7	67.6	16.0
23	CH_3	0.245	−106.84	577.7	50.5	63.3	13.2
24	CH_3O	0.211	−102.00	600.5	55.0	67.4	15.0
25	CH_3S	0.157	−109.54	586.6	53.7	65.8	14.8
Ar_3SnNCS							
26	H	0.214	−118.52	$^1J(^{119}Sn-^{14}N) = 90.2$ Hz			
27	F	0.187	−116.6	broad peak			
28	Cl	0.226	−120.4				
29	CH_3	0.222	−107.25	$^1J(^{119}Sn-^{14}N) = 89.7$ Hz			
30	Ph	0.071	−112.61	$^1J(^{119}Sn-^{14}N) = 68.6$ Hz			

[a] Data from carbon-13 spectra. [b] Concentration $\leqslant 0.05$ M.

stituents is also observed for Ar_3SnX but the correlation is now with either Hammett (σ_p) or Taft (σ_p°) constants. For the iodide system including all data points gives a good correlation with σ_p values ($r = 0.956$) but not with the Taft constants ($r = 0.882$). Again omitting the phenyltin point improves both correlations, these being the lines in Fig. 2. However, as iodide in Ar_3SnX is replaced by bromide and then chloride the correlations with either σ_p or σ_p° become increasingly less quantitative (X = Br: σ_p, $r = 0.91$; σ_p°, $r = 0.85$; X = Cl: σ_p, $r = 0.85$; σ_p°, $r = 0.78$), even with the Y = H datum point omitted. In contrast, the few data points for the Ar_3SnNCS system show excellent correlation ($r < 0.97$) with both σ_p and σ_p°, although the phenyltin point must again be omitted for this to occur.

Some of the above anomalies disappear with DSP analysis as shown in Table 3, using two sets of substituent parameters, (σ_I, σ_R) and (σ_I, σ_R°). To test the correlations Table 3 includes not only values of the correlation coefficient ($r > 0.95$) [20] but also of the 'goodness-of-fit' parameter, $f = (SD/RMS)$ [21], where *RMS* is the root-mean-square size of the experimental data, in this case the sets of ($\delta_{Sn} - C$) or ($\delta_{Sn} - C_0$) values. A decreasing f value shows the correlations become

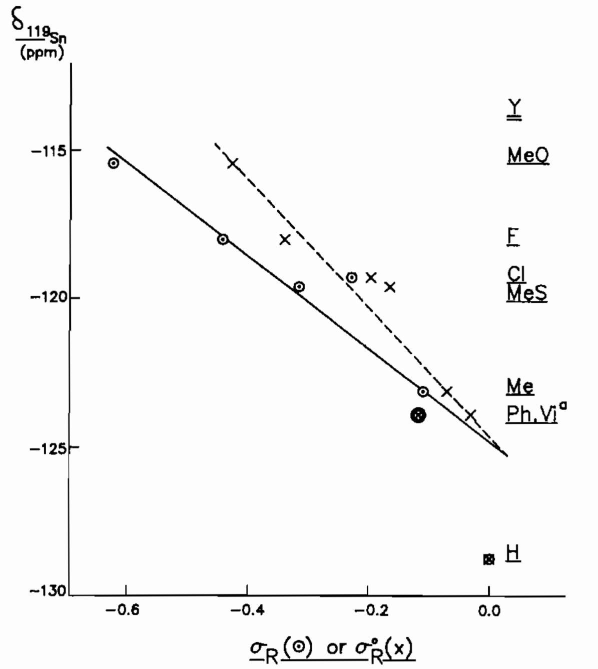


Fig. 1. Tin-119 chemical shifts for $(p\text{-}YC_6H_4)_4Sn$ in $CDCl_3$ plotted against σ_R (⊙) or σ_R° (×); straight lines (——) (r = 0.957) or (– – –) (r = 0.951) respectively, omit the Ph_4Sn datum point. [a]Ref. 18.

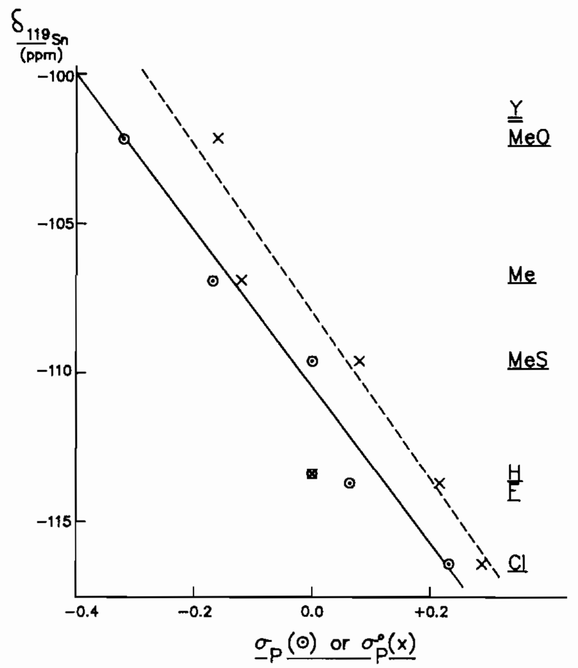


Fig. 2. Tin-119 chemical shifts for $(p\text{-}YC_6H_4)_3SnI$ in $CDCl_3$ plotted against σ_p (⊙) or σ_p° (×); straight lines (——) (r = 0.979) or (– – –) (r = 0.968) respectively, omit the Ph_4Sn datum point.

TABLE 3. Tin-119 Chemical Shift Regression Analysis Parameters[a]

	ρ_I	ρ_R	C	r^b	SD^c	f^d	n^e
(a) $\delta_{^{119}Sn} = \rho_I\sigma_I + \rho_R\sigma_R + C$							
Ar_4Sn	3.73	−13.24	−125.0	0.976	0.668	0.12	7^f
Ar_3SnCl	−13.86	−24.07	−39.3	0.976	0.866	0.15	5
Ar_3SnBr	−16.29	−23.31	−55.6	0.980	0.795	0.15	5
Ar_3SnI	−25.44	−24.81	−111.0	0.986	0.850	0.17	5
	−24.63	−26.93	−112.2	0.978	1.03	0.20	6^g
Ar_3SnNCS	−31.43	−25.55	−111.7	0.997	0.369	0.07	4
	ρ_I	ρ_R	C°	r^b	SD^c	f^d	n^e
(b) $\delta_{^{119}Sn} = \rho_I\sigma_I + \rho_R\sigma_R^\circ + C^\circ$							
Ar_4Sn	1.67	−19.72	−124.6	0.954	0.915	0.18	7^f
Ar_3SnCl	−18.74	−38.26	−38.8	0.985	0.687	0.12	5
Ar_3SnBr	−21.01	−37.02	−55.1	0.988	0.627	0.14	5
Ar_3SnI	−30.57	−39.69	−110.5	0.996	0.461	0.09	5
	−29.92	−43.48	−111.9	0.981	0.944	0.19	6^g
Ar_3SnNCS	−34.92	−40.74	−112.4	0.988	0.766	0.15	4

[a]Values for σ_I, σ_R, and σ_R° are from ref. 19. [b]Multiple correlation coefficient. [c]Standard deviation of residuals. [d]'Goodness-of-fit' parameter – see text. [e]Number of compounds – omitting the phenyltin datum point. [f]Includes $\delta_{^{119}Sn}$ = −123.90 ppm for $(p\text{-}CH_2CHC_6H_4)_4Sn$ [18]. [g]Includes the Ph_3SnI datum point.

moderately good ($f < 0.2$) and then excellent (<0.1) although $f < 0.06$ has been suggested as the criterion required for an acceptable fit of the data with the given substituent constants [22].

The DSP analysis for Ar_4Sn confirms the very strong dependence of the tin-119 chemical shift on the resonance parameter which contrasts with the earlier report [6] on *para*-substituted phenyltrimethylstannanes for which resonance susceptibility was quite low. Similarly for Ar_3SnI, the very similar resonance and inductive susceptibility parameter values are consistent with the single parameter relations shown in Fig. 2. However, with Ar_3SnBr and Ar_3SnCl systems, the influence of the inductive parameter (σ_I) decreases relative to that of σ_R or σ_R°, although it is still significant, showing why single-parameter correlations were inadequate for these systems. Unfortunately, while some anomalies in the correlations are removed by DSP regression analysis, data points for the phenyl systems (Y = H) still show surprising deviations ($r < 0.95$) and the DSP analyses in Table 3 omit these data, a procedure for which there is a precedent [23]. Only for Ar_3SnI does including the Y = H datum point still give satisfactory DSP correlations.

Tin-119 resonances for Ph_3SnNCS and $(p\text{-}Tol)_3SnNCS$ (Fig. 3) are observed as triplets arising from $^{119}Sn-^{14}N$ coupling, for which only two other examples have been reported, $Sn(NCS)_6^{2-}$ [24] and $(C_6H_{11})_3SnNCS$ [25]. The spectrum shown here represents a partially collapsed triplet ($^1J(^{119}Sn-^{14}N) \sim 90$ Hz) compared with the 'ideal' of three equal peaks [25], but in both cases the environment around the nitrogen atom must be fortuitously symmetric for tin–nitrogen coupling to be seen. Replacement of *para*-H by phenyl causes further broadening so the triplet is almost undetectable ($^1J(^{119}Sn-^{14}N) \sim 70$ Hz) while further collapse means the tin resonances for $(p\text{-}YC_6H_4)_3SnNCS$ (Y = F or Cl) are broad featureless humps, closer to the single line which is usually observed, e.g. for Bu_3SnNCS [24] as the environment of the nitrogen atom is usually sufficiently asymmetric to preclude observation of tin–nitrogen spin coupling in most cases.

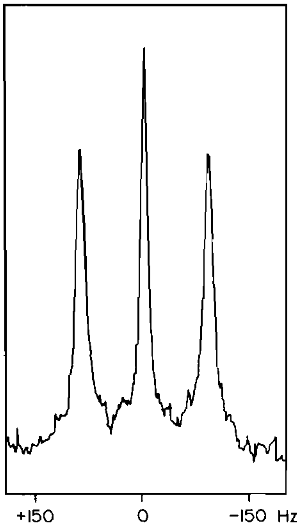


Fig. 3. Tin-119 spectrum of $(p\text{-}Tol)_3SnNCS$ (0.222 M) in $^5J(^{119}Sn-^{19}F)$:

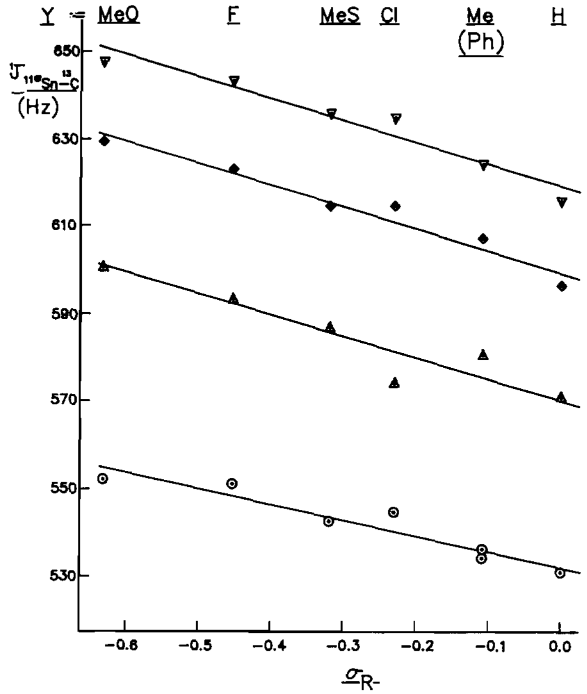


Fig. 4. $^1J(^{119}Sn-^{13}C_{ipso})$ values for Ar_4Sn (◎), Ar_3SnI (▲), Ar_3SnBr (◆) and Ar_3SnCl (▼) plotted against σ_R, straight lines have (◎) $r = 0.960$, (▲) $r = 0.958$, (◆) $r = 0.978$ and (▼) $r = 0.968$.

(b) Carbon-13 Data

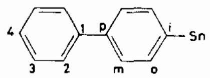
The $^nJ(^{119}Sn-^{13}C)$ values reported in Table 2 show the trend ($Ar_4Sn < Ar_3SnI < Ar_3SnBr < Ar_3SnCl$) associated with the increasing 5s-character of the tin hybrid orbital forming the Sn–C bond [26]. One-bond coupling constants for each aryltin system correlate well with the same substituent parameters either σ_R or σ_R° (Fig. 4). This implies that the significant substituent effect on tin–carbon spin-coupling is the same in all cases, that is on the 2s-character of the carbon hybrid orbital used to form the Sn–C bond. This is in fact the only change possible for the Ar_4Sn series.

Carbon-13 chemical shift data (Table 4) show the same qualitative changes on varying the *para*-substituent with the resonance parameter σ_R° as those reported earlier [27] for several series of *para*-disubstituted benzenes. No DSP analysis of the data was attempted since the range of substituents used here was insufficient for effective comparisons with the earlier work especially as non-linear substituent effects are involved. However, the data show the *para*-substituents are acting as expected displacing the *ipso*-carbon chemical shift to lower frequency (indicating an increase in the π-electron density at this site) consistent with more negative σ_R° values notwithstanding the concurrent shift to higher frequency of the tin resonance.

TABLE 4. ^{13}C NMR Chemical Shifts (ppm) of Aryltin Compounds in $CDCl_3$

No^a	*ipso*	*ortho*	*meta*	*para*	Other chemical shifts (ppm) and coupling constants (Hz)
1	138.04	137.31	128.69	129.17	
2	132.12	138.68	116.25	164.10	$\delta(^{19}F)$: −111.29; $^5J(^{19}Sn-^{19}F)$: 10.0 $^1J(^{19}F-^{13}C)$: 248.6; $^2J(^{19}F-^{13}C)$: 19.5; $^3J(^{19}F-^{13}C)$: 5.9; $^4J(^{19}F-^{13}C)$: 4.0
3	134.62	138.10	129.19	136.27	
4	134.46	137.18	129.39	138.76	$\delta(^{13}C)$ 21.48(CH_3)
5	128.74	138.26	114.45	160.47	$\delta(^{13}C)$: 54.91(CH_3O)
6	133.24	137.33	126.35	140.28	$\delta(^{13}C)$: 15.18(CH_3S)
7^b	136.66	137.75	127.49	142.14	$\delta(^{13}C)$: 141.04(C(1)), 128.91(C(2)), 127.25(C(3)), 127.58(C(4))
8	137.39	136.18	129.18	130.51	
9	131.91	137.89	116.71	164.64	$\delta(^{19}F)$: −108.90; $^5J(^{119}Sn-^{19}F)$: 13.4; $^1J(^{19}F-^{13}C)$: 250.6 $^2J(^{19}F-^{13}C)$: 20.2; $^3J(^{19}F-^{13}C)$ 7.2; $^4J(^{19}F-^{13}C)$: 4.1
10	134.48	137.10	129.55	137.46	
11	133.85	136.03	129.88	140.44	$\delta(^{13}C)$. 21.52(CH_3)
12	128.08	137.41	114.92	161.40	$\delta(^{13}C)$: 55.11(CH_3O)
13	132.56	136.17	126.40	142.17	$\delta(^{13}C)$: 15.05(CH_3S)
14	137.16	136.37	129.32	130.58	
15	131.50	137.89	116.62	164.52	$\delta(^{19}F)$: −109.10; $^5J(^{119}Sn-^{19}F)$: 13.7; $^1J(^{19}F-^{13}C)$: 250.5; $^2J(^{19}F-^{13}C)$: 19.6; $^3J(^{19}F-^{13}C)$: 7.5; $^4J(^{19}F-^{13}C)$: 3.9
16	134.15	137.15	129.51	137.37	
17	133.51	136.08	129.84	140.35	$\delta(^{13}C)$: 21.52(CH_3)
18	128.10	137.77	115.23	161.69	$\delta(^{13}C)$: 55.48(CH_3O)
19	132.25	136.24	126.37	142.06	$\delta(^{13}C)$: 15.07(CH_3S)
20	136.30	136.30	129.03	130.24	
21	130.82	137.91	116.46	164.39	$\delta(^{19}F)$: −109.52; $^5J(^{119}Sn-^{19}F)$: 13.8; $^1J(^{19}F-^{13}C)$: 251.7; $^2J(^{19}F-^{13}C)$: 20.2; $^3J(^{19}F-^{13}C)$: 7.5; $^4J(^{19}F-^{13}C)$: 3.6
22	132.11	135.87	128.03	135.80	
23	132.83	136.16	129.72	140.14	$\delta(^{13}C)$: 21.47(CH_3)
24	127.14	137.46	114.76	161.22	$\delta(^{13}C)$: 55.11(CH_3O)
25	131.63	136.34	126.33	141.83	$\delta(^{13}C)$: 15.11(CH_3S)

^{a}See Table 2.

b 

Discussion

Although the range of substituents used in this work does not correspond to that currently recommended [28] to test statistically valid correlations, the results reported here are sufficient to show that the trends in ^{119}Sn chemical shifts associated with substituents on a specific organic group, in this case phenyl, cannot be generalised for all the organotin systems containing the same organic moiety. Even for the same organotin system, $RSnMe_3$, attempts to examine the sensitivity of ^{119}Sn chemical shifts to polar influences noted first with R = Ph [6] by using carefully selected R groups [29–31] incorporating tactical structural and/or electronic changes to determine the factors involved, have proved inconclusive.

The tendency for Ar_4Sn tin chemical shifts to move to higher frequencies with π-electron donor substituents in the *para*-position, is unexpected since these substituents clearly increase the π-electron density at the *ipso*-carbon atoms – as indicated by carbon-13 data. This anomaly parallels the well known shift to lower frequencies (greater shielding) as alkyl groups in organotins are replaced by the more electronegative aryl, heteroaryl, vinyl and/or ethynyl units which should cause inductive electron withdrawal from the tin [32–34]. It has been suggested that these 'π-electron rich' systems may indulge in $p_\pi \rightarrow d_\pi$ interactions with the tin-5d orbitals, increasing σ-electron withdrawal as the groups become more electronegative thus encouraging further synergic $p_\pi \rightarrow d_\pi$ backdonation [35, 36]. Our results contradict this picture since the *para*-group that provides the most π-electron density at the *ipso*-carbon causes the greatest shift to higher frequency. Indeed, quantum mechanical calculations show little interaction occurs between tin-5d and carbon-2p orbitals in the ground states of either methyltin [37] or phenyltin [38] systems.

Shielding of heavy atom nuclei, including tin, is considered [32, 33, 39] to be dominated by the paramagnetic term, σ^p, often given by the simplified relation

$$\sigma^p = \frac{\mu_0 e^2 \hbar^2}{-6\pi m^2 \Delta E} (\langle r^{-3} \rangle_{np} P_u)$$

assuming that for four-coordinate tin compounds, d-electron involvement may be ignored if there is no π-bonding. The term P_u, the electron imbalance associated with the tin-5p orbitals, is strongly influenced by changes in the electronegativities of R or X attached to tin in asymmetric R_4SnX_{4-n} systems. For symmetric R_4Sn, P_u is unlikely to vary much as R is changed, while $\langle r^{-3}\rangle_{5p}$, where r_{5p} is the position of the 5p electron with respect to the tin nucleus, depends mainly on the effective nuclear charge, Z_{eff}, of tin for the electron in question, and is also unlikely to change significantly for a series of R_4Sn compounds. However, this term may account for the shift to lower frequency (increased shielding) when the coordination number of tin increases from four to five or six. The third term ΔE, the average electronic excitation energy, is usually considered to be constant for series of related molecules. However, Mitchell *et al.* [40] observing $\delta(^{207}Pb)$ values to be temperature dependent, proposed this assumption might be invalid. Tin-119 chemical shifts for $(p\text{-}YC_6H_4)_4Sn$ (Y = H, CH_3, CH_3O, CH_3S) correlate well with $\delta(^{207}Pb)$ data for the lead analogues [40, 41], the relation, $\delta(^{207}Pb) = 1.98\ \delta(^{119}Sn) + 76.7$ (r = 0.995) being consistent with the more general correlation observed for ^{119}Sn and ^{207}Pb chemical shifts [42]. Thus the variation of $\delta(^{119}Sn)$ values noted for R_4Sn may wll involve also changes in ΔE.

Recent calculations for phenyltin systems [38] show low-lying unoccupied molecular orbitals involving contributions from tin-5d and carbon-2p orbitals of the aryl groups which if filled can give rise to low energy excited states of these molecules. Further interaction with orbitals from the group in the *para*-position may lower the excited state energies even more, reducing ΔE, thereby increasing the paramagnetic contribution, and thus shifting the ^{119}Sn resonance to higher frequency [43]. Changing ΔE values have been invoked to account for the wide variations observed in nitrogen chemical shifts [44] as well as in the NMR spectra of transition metal nuclei [45]. Of particular interest is the effect of changing X in a series of symmetric isostructural heteropolytungstates, $[X^{n+}W_{12}O_{40}]^{(8-n)-}$, for which it was found that $\delta(^{183}W)$ varied linearly with λ, the wavelength of the lowest energy UV transition for these ions [46]. Thus where chemical shift variation is due to changes in the molecule or complex ion distant from the nucleus being studied, the possibility that ΔE may vary cannot be excluded.

The larger substituent effects, including dependence on both inductive and resonance parameters, observed for the Ar_3SnX (X = Cl, Br, I) series, imply that a second mechanism overlaps that which occurs in the tetra-aryltin system. For the tri-aryltin halides, electron donor *para*-substituents will further enhance the ionic character of the Sn–X bond in these molecules and shift the tin resonance to higher frequency [47], as is observed here. The less anomalous position of hydrogen as a *para*-substituent particularly with X = I, is consistent with this being a ground state substituent effect.

Even with the assumption that tin-119 shielding is dominated by the paramagnetic contribution (σ^p), many factors can influence tin chemical shifts. The results presented here for the substituent effects on tin chemical shifts in Ar_4Sn and Ar_3SnX, as well as the $ArSnMe_3$ system reported earlier, show no single mechanism applies. It seems likely that each system must be considered on an individual basis while detailed quantum mechanical calculations will be required to show the effect of changes in the *para*-substituents on the ground state and/or excited states in each series and the pathway for the substituent effect for the given system.

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