

polymer was accomplished by filtration; however, the $(\text{Ph}_3\text{P})_2\text{Ni}(\text{CO})_2$ had decomposed during the period of hydrogenation when a temperature of 165° was employed.

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Tin-119 Chemical Shifts of Ortho, Meta, Para, 2,6-, and Polysubstituted Aryltrimethyltin Derivatives and Related Organotin Compounds^{1a}

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Abstract: Tin-119 chemical shifts for 15 meta and para, 10 ortho, 7 2,6-disubstituted, and seven miscellaneous polysubstituted aryltrimethyltin compounds along with the shifts of 15 additional aliphatic organotin compounds have been recorded by direct observation at 37.27 MHz in the continuous wave mode. Although the chemical shift response of the ten nuclei which have thus far been incorporated into various series of phenyl compounds with respect to electron withdrawal is mixed, i.e., about half the series studied fail to change in the expected downfield direction with electron withdrawal, the tin chemical shifts show excellent correlations ($r > 0.97$) with σ_1 and σ_R° values, with the shifts changing in the anticipated manner. The shift differences, $\Delta\delta$, imposed by moving the substituent from the para to the ortho position range from the small changes induced by the halogen and trifluoromethyl groups to $\Delta\delta = -16.3$ ppm for the dimethylamino group. These changes are accentuated in the 2,6-derivatives. Upfield shifts of the alkyl group-bearing substituents are interpreted in terms of steric compression and angular distortion produced in the bonds to tin, while dispersion forces may account for the downfield shifts of the ortho and 2,6-disubstituted halo derivatives. Small tin-119m Mössbauer quadruple splittings, observed for these derivatives are also found for the para compounds and are interpreted in terms of electronegativity. $[J(^{119}\text{Sn}-^{19}\text{F})]$ coupling constants for the ortho, meta, and para derivatives have similar small values, and large upfield shifts characteristic of higher coordination at tin are lacking. The observed effects of introducing saturated carbon atoms in aliphatic derivatives α , β , and γ to tin on the shifts are similar to those for carbon-13 and the heavier nuclei, with α - and β -substitution producing a downfield shift and γ -substitution producing an upfield shift, suggesting a similar mechanism governing the shifts in each case. The shift of the *syn*-7-trimethyltinborbornene lies 14.3 ppm to lower field than in the anti isomer suggesting interaction with the double bond. Large downfield shifts are also seen when the tin atom is incorporated into a small ring. Unsaturated groups induce large upfield shifts when directly attached to tin.

Since the first publication by Burke and Lauterbur² in 1961, there have been over 40 research papers reporting tin-119 NMR chemical shift data,³ and an excellent review.⁴ Tin chemical shifts are now known to range from -1712 for SnI_4 in a 1:1 mixture with SnCl_4 to $+199$ ppm for diethyltin thioglycolate,⁵ with respect to tetramethyltin as a standard, or 1911 ppm overall (or to -662 for $\text{CH}_3\text{SnBr}_2^{2-}$ in water,⁶ for a range of 861 ppm for organotin derivatives, or to -282 for triethyltin hydride,³ for a range of 481 ppm for four-coordinated organotin species). Yet there is no satisfactory answer to the question of the effect of electron withdrawal on tin chemical shifts.

In an attempt to settle this question, we report in this paper tin chemical shifts for 15 meta and para, 10 ortho, 7 2,6-disubstituted, and 7 miscellaneous and polysubstituted aryltrimethyltin compounds, along with the shifts of 15 additional organotin species.

Results

The reader of the tin chemical shift literature is cautioned to note carefully the sign convention used in tabulating the data. While the use of tetramethyltin as a standard dates from the early work of Hunter and Reeves,⁷ it is only recently that the shift sign conventions of the heavier nu-

Table I. Tin-119 Chemical Shifts of *m*- and *p*-RC₆H₄Sn(CH₃)₃ (50% v/v in CCl₄) ±0.2 ppm

No. ^a	R	δ(¹¹⁹ Sn) ^b
1	<i>m</i> -CF ₃ ^c	-23.9 ^d
2	<i>m</i> -Cl	-24.5
3	<i>m</i> -F ^e	-25.0 ^d
4	<i>p</i> -Br	-25.0
5	<i>p</i> -Cl	-25.6
6	<i>p</i> -F ^f	-25.9 ^{d,g}
7	<i>m</i> -OCH ₃	-28.0
8	<i>p</i> -OC ₂ H ₅	-28.6
9	<i>p</i> -OCH ₃	-28.8
10	<i>p</i> -CH ₃	-29.9
11	<i>m</i> -CH ₃	-29.9
12	<i>p</i> -N(CH ₃) ₂	-30.2 ^h
13	H	-30.3 ⁱ
14	<i>p</i> -Sn(CH ₃) ₃	-30.5 ^j
15	<i>p</i> - <i>t</i> -C ₄ H ₉	-30.6

^aListed in order of increasing upfield shift. ^bA negative sign indicates a resonance upfield of tetramethyltin. ^c $|^4J(^{119}\text{Sn}-\text{C}-\text{C}-\text{C}-^{19}\text{F})| = 4.0$ Hz. ^dAveraged value because of the coupling to fluorine-19. ^e $|^4J(^{119}\text{Sn}-\text{C}-\text{C}-\text{C}-^{19}\text{F})| = 22.0$ Hz. ^f $|^5J(^{119}\text{Sn}-\text{C}-\text{C}-\text{C}-^{19}\text{F})| = 9.2$ Hz. ^gListed as -25.9 ppm in cyclohexane solvent in ref 10. ^hListed as 30.0 ppm in ref 10 in cyclohexane solvent. ⁱListed as -30 ppm run as the neat liquid in ref 7. ^jListed as -29.0 ppm run 20% in CH₂Cl₂ in ref 3.

Table II. Tin-119 Chemical Shifts of *o*-RC₆H₄Sn(CH₃)₃ (50% v/v in CCl₄) ±0.2 ppm

No. ^a	R	δ(¹¹⁹ Sn) ^b
1	CF ₃ ^c	-16.6 ^d
2	Cl	-24.2
3	F ^e	-28.5 ^d
4	H	-30.3 ^f
5	Sn(CH ₃) ₃	-33.8
6	CH ₃	-34.0 ^g
7	OCH ₃	-34.6
8	C ₂ H ₅	-35.1
9	OC ₂ H ₅	-35.4
10	N(CH ₃) ₂	-46.3

^aListed in order of increasing upfield shift. ^bA negative sign indicates a resonance upfield of tetramethyltin. ^c $|^4J(^{119}\text{Sn}-\text{C}-\text{C}-\text{C}-^{19}\text{F})| = 2.5$ Hz. ^dAveraged value because of the coupling to fluorine-19. ^e $|^3J(^{119}\text{Sn}-\text{C}-\text{C}-^{19}\text{F})| = 64.8$ Hz. ^fListed as -30.3 ppm run as the neat liquid in ref 7. ^gListed as -33.0 ppm run 20% in CH₂Cl₂ in ref 3.

clei^{8,9} have begun to fall into agreement with that used in proton NMR, where resonances upfield of the TMS standard are negative. In tin NMR papers submitted up to the spring of 1972 with one Russian exception,¹⁰ resonances to high field of the tetramethyltin standard are listed as positive, and a review article which tabulates the data available to May 1973⁴ follows this convention. After March 1972, all papers submitted have listed upfield resonances as negative. In many cases it is extremely difficult or impossible to tell from the information given which sign convention is in use. Comparisons of literature data close to zero shift (tetramethyltin) are particularly hazardous. We will in this paper adopt the convention that shifts upfield of the standard are negative, contrary to our previous practice.^{3,11}

Table I lists tin-119 chemical shift values in ppm for 15 meta and para substituted phenyltrimethyltin compounds in order of increasing upfield shift with respect to tetramethyltin as standard. The values of absolute frequency, Ξ , defined as the resonant frequency in a magnetic field of strength such that Si(CH₃)₄ gives a proton resonance of exactly 100 MHz, have previously been used.¹² The values of the *p*-fluoro,¹⁰ *p*-dimethylamino,¹⁰ and *p*-trimethyltin³ derivative, and the parent phenyltrimethyltin⁷ have been recorded previously; however, all were redetermined in this

Table III. Tin-119 Chemical Shifts of 2,6-R₂C₆H₃Sn(CH₃)₃ and Other Di- and Trisubstituted Aryltrimethyltins (50% v/v in CCl₄) ±0.2 ppm

No. ^a	R	δ(¹¹⁹ Sn) ^b
1	2,6-CF ₃ ^c	-8.9 ^d
2	2,6-Cl	-11.6
3	2,6-F ^e	-28.4 ^d
4	H	-30.3 ^f
5	2,6-OCH ₃	-43.7
6	2,6-OC ₂ H ₅	-46.0
7	2,6-CH ₃	-51.4
8	2,4-CF ₃ ^g	-6.6
9	2,4-CH ₃	-34.0
10	2,3-CH ₃	-34.0 ^h
11	3,4-CH ₃	-30.9
12	3,5-CF ₃ ⁱ	-17.0 ^d
13	2,4,6-OCH ₃	-43.8
14	2,4,6-CH ₃	-50.0 ^h
15	2,3,4,5,6-Cl	+123 ^j

^aListed in order of increasing upfield shift within substitutional categories. ^bA negative sign indicates a resonance upfield of tetramethyltin. ^c $|^4J(^{119}\text{Sn}-\text{C}-\text{C}-\text{C}-^{19}\text{F})| = 1.8$ Hz. ^dAveraged value because of the coupling to fluorine-19. ^e $|^3J(^{119}\text{Sn}-\text{C}-\text{C}-^{19}\text{F})| = 42.7$ Hz. ^fListed as -30.3 ppm run as the neat liquid in ref 7. ^gThe two couplings to fluorine could not be resolved. ^hFrom ref 3, 50% in CH₂Cl₂. ⁱ $|^5J(^{119}\text{Sn}-\text{C}-\text{C}-\text{C}-^{19}\text{F})| = 2.9 \pm 0.7$ Hz. ^jFrom ref 3, saturated solution in CH₂Cl₂.

Table IV. Tin Chemical Shift Regression Analysis Parameters^a

	ρ_I^b	ρ_R^b	C ^c	r ^d	S ^e	n ^f
Ortho	29.0	34.5	-29.4	0.990	1.74	7
Meta	11.9	2.95	-29.7	0.983	0.700	6
Para	10.2	2.93	-29.6	0.973	0.665	7

^aLack of σ_I and σ_R° values for -Sn(CH₃)₃, -*t*-C₄H₉, -OC₂H₅, and -C₂H₅ excludes these derivatives from the regression analysis. ^bParameters of the equation $\delta = \rho_I\sigma_I + \rho_R\sigma_R^\circ + C$ using σ_I and σ_R° values from ref 19. ^cIntercept. ^dMultiple correlation coefficient. ^eStandard deviation of residuals. ^fNumber of compounds.

study. From the *m*-CF₃ at -23.9 to the *p*-*t*-C₄H₉ at -30.6 ppm, the range of meta and para substituents available taken together imposes an overall change of 6.8 ppm on the position of the tin-119 resonance.

Table II lists values for ten ortho-substituted derivatives in increasing upfield shift order. Only the *o*-methyl³ and the parent phenyltrimethyltin⁷ compound had been recorded previously, but both were redetermined for this study. From the *o*-CF₃ at -12.6 to the *o*-dimethylamino at -46.3 ppm, the range of ortho substituents available imposes an overall change of 33.8 ppm on the tin resonance.

Table III lists values for seven 2,6-disubstituted derivatives in increasing upfield shift order for seven miscellaneous di- and trisubstituted compounds. Values for the 2,3-di-, and 2,4,6-trimethyl derivative were taken from ref 3 as was the value for perchlorophenyltrimethyltin. From the CF₃ at -8.9 to the CH₃ at -51.4 ppm, 2,6-disubstitution imposes a change of 42.5 ppm on the tin resonance. Rendering the same change at the 2,4-positions imposes a change of only 27.4 ppm on the tin shift. The resonance of the perchlorophenyltrimethyltin compound lies in another region entirely, downfield of tetramethyltin.

The tin chemical shift relationship with the σ_I and σ_R° substituent constant values meets the requirements stated by Miller et al.^{13,14} that data for NMR correlations be derived from measurements on large numbers of representative compounds, giving correlation coefficients >0.95. The regression analysis data are listed in Table IV for the ortho, meta, and para series.

Table V. Tin-119 Mössbauer Data at 77 K for $RC_6H_4Sn(CH_3)_3^a$

R	δ (± 0.06), mm/sec	Δ (± 0.12), mm/sec	Γ_1^b	Γ_2
<i>m</i> -Cl	1.28		1.33	
<i>m</i> -F	1.32		1.27	
<i>p</i> -Br	1.25		1.35	
<i>p</i> -Cl ^c	1.24		1.72	
<i>p</i> -F ^d	1.31		1.75	
<i>m</i> -OCH ₃	1.26		1.18	
<i>p</i> -OC ₂ H ₅	1.29		1.09	
<i>p</i> -OCH ₃ ^e	1.24		1.13	
<i>p</i> -CH ₃ ^f	1.28		1.16	
<i>m</i> -CH ₃	1.29		1.11	
<i>p</i> -N(CH ₃) ₂ ^g	1.25		1.16	
H ^h	1.32		1.15	
<i>p</i> -Sn(CH ₃) ₃	1.22		1.44	
<i>p</i> - <i>i</i> -C ₄ H ₉ ⁱ	1.30		1.18	
<i>o</i> -CF ₃ ^j	1.25	0.74	0.68	0.52
<i>o</i> -Cl	1.24		1.30	
<i>o</i> -F	1.29		1.84	
<i>o</i> -Sn(CH ₃) ₃	1.28		1.35	
<i>o</i> -CH ₃	1.27		1.04	
<i>o</i> -OCH ₃	1.22		1.18	
<i>o</i> -C ₂ H ₅	1.27		1.44	
<i>o</i> -OC ₂ H ₅	1.22		1.12	
<i>o</i> -N(CH ₃) ₂	1.30		1.03	
2,6-CF ₃	1.26	0.90	1.13	1.04
2,6-Cl	1.27	0.87	0.88	0.96
2,6-F	1.32	1.00	1.24	1.11
2,6-OCH ₃	1.28		1.30	
2,6-OC ₂ H ₅	1.20		1.30	
2,6-CH ₃	1.33		1.48	
2,4-CF ₃	1.22		1.74	
2,4-CH ₃	1.23		0.94	
3,4-CH ₃	1.30		1.42	
3,5-CF ₃	1.34	0.61	1.51	1.01
2,4,6-OCH ₃	1.21		1.57	
2,3,4,5,6-Cl ^k	1.32	1.09		

^a Vs. Ba^{119m}SnO₃ (New England Nuclear Corp.) held at ambient temperature. ^b Line width ± 0.06 mm/sec. ^c Listed as 1.34 ± 0.05 mm/sec in ref 15. ^d Listed as 1.23 ± 0.03 mm/sec in ref 16. ^e Listed as 1.30 ± 0.05 mm/sec in ref 15. ^f Listed as 1.22 ± 0.03 mm/sec in ref 16. ^g Listed as 1.30 ± 0.05 mm/sec in ref 15. ^h Listed as 1.16 ± 0.03 in ref 17, as 1.25 ± 0.05 in ref 18, and as 1.26 ± 0.05 in ref 15. ⁱ Listed as 1.28 ± 0.05 mm/sec in ref 15. ^j Listed as 1.16 ± 0.03 , 0.66 ± 0.03 mm/sec in ref 16. ^k Reference 17.

Table V lists tin-119m Mössbauer data for the compounds studied, grouped by category as shown in Tables I, II, and III, and listed in order of increasing upfield tin-119 NMR chemical shift as in these tables. Some Mössbauer data for the parent phenyltrimethyltin and its derivatives have been published previously.¹⁵⁻¹⁸ The F, Cl, and CF₃ substituents give rise to small quadrupole splittings (QS) in some circumstances. It should be kept in mind that in the case of potentially tiny QS doublet spectra, computer fitting can be forced to yield a QS value from a broad line. Such borderline cases are found for the *p*-chloro, *p*-fluoro, and *o*-fluoro derivatives with line widths, $\Gamma = 1.72, 1.75,$ and 1.88 mm/sec, respectively. Curve fitting the spectrum of the *o*-trifluoromethyl derivative as a doublet gave unrealistically narrow line widths (0.68, 0.52 mm/sec).

Discussion


A fundamental question with regard to nonprotonic NMR chemical shifts is their response to electron withdrawal. While current theories of shielding do not permit satisfactory interpretation of individual chemical shift values, it is expected that the spin nucleus will become more shielded as the electron-releasing power of substituent

groups increases, and the chemical shift should move progressively to higher field. Available data from compounds in which drastic electronegativity changes are imposed at the heavier elements present a confused picture, and we will confine our discussion to systems in which electron demand is smoothly varied systematically through the use of substituted phenyl groups.

Understanding the data for the substituted phenyl derivatives of the various spin nuclei requires a knowledge of the range of shift imposed by the available substituent groups, the direction of the imposed shift, and whether the chemical shift data correlate with substituent constants or with similar shift data for other nuclei (the Taft σ_I and σ_R° parameters are themselves derived from fluorine-19 chemical shift data in part).¹⁹ The tin data must be viewed against the background of available results on the substituted phenyl derivatives of other spin nuclei. Unfortunately, even in these well-regulated systems, the results are contradictory. Table VI lists the results of studies on ten NMR nuclei: hydrogen-1,²⁰ carbon-13,²¹⁻²² nitrogen-14,^{23,25-26} nitrogen-15,^{24,27} fluorine-19,²⁸ silicon-29,^{29,30} phosphorus-31,³¹ tin-119, mercury-199,^{8,9} and lead-207.^{8,9} (including our results for the phenyltrimethyltins) which have been incorporated into various series of para-, meta-, and ortho-substituted phenyl compounds. Table VI lists the number of compounds, *n*, examined in each category, the range of shifts observed, Δ , in ppm, the substituents establishing the endpoints of the range, $+\sigma$ and $-\sigma$, and whether the general trend followed by the data was according to that expected on the basis of the Hammett σ constants, (positive) or opposite to it (negative). Plots or stated correlations in the literature seldom include correlation coefficients or other regression analysis data, and no attempt has been made here to correlate the recorded chemical shifts with Hammett or other substituent constants. For the para derivatives the chemical shift range encompassed increases $^1H < ^{13}C < ^{29}Si < ^{15}NO_2 < ^{14}NO_2 < ^{119}Sn < ^{31}P < ^{207}Pb < ^{14}NH_2 < ^{15}NH_2 < ^{199}Hg$, for the meta derivatives $^1H < ^{29}SiF_3 < ^{13}C < ^{29}Si(CH_3)_3 < ^{19}F < ^{14}N < ^{31}P < ^{15}N < ^{119}Sn < ^{207}Pb$, and for the ortho derivatives recorded $^1H < ^{29}Si(CH_3)_3 < ^{14}N < ^{13}C < ^{19}F < ^{119}Sn$. The change in shift imposed by the replacement of the *o*-dimethylamino by the *o*-trifluoromethyl group at tin is the largest yet recorded for any such replacement at a single position. For three other nuclei as well (1H , ^{13}C , and $^{29}Si(CH_3)_3$), the magnitudes of the shift values are ortho \gg meta and para, but for ^{19}F the magnitudes are ortho $>$ para \gg meta, and for $^{14}NH_2$ and $^{15}NH_2$, para \gg meta.

Clearly, of the 33 series represented in Table VI, 14 fail to change with electron withdrawal in the anticipated manner. The examples in which NMR resonances respond to electron withdrawal through the phenyl group by shifting upfield, opposite to that expected, include meta- ^{13}C and meta- and para- ^{31}P and ^{207}Pb .

Recent discussion has focused attention on the change in trend which is experienced by silicon-29 resonances in phenyltrimethylsilanes²⁹ in which the ^{29}Si resonances respond in the expected manner, and in phenyltrifluorosilanes³⁰ in which increased electron withdrawal results in upfield shifts. A theoretical model has been applied which attempts to rationalize the two opposite trends on the basis of the total charge on the silicon atom. The theory asserts that an atom with higher total charge (one with weakly electronegative ligands, e.g., $Si(CH_3)_3$) will tend to experience deshielding on electron withdrawal, but that the opposite can be expected for an atom with a lower total charge (one with strongly electronegative ligands, e.g., SiF_3).³² While apparently true for the silicon-29 data, a reversal is seen between the substituted anilines (positive) and nitrobenzenes.¹⁴ N (negative). The more electropositive lead atom responds

Table VI. Shift Trends in E-

E	Position	n^a	$+\sigma^b$	$-\sigma^b$	Δ^c	Trend ^d	Ref
¹ H-	Para	10	-NO ₂	-NH ₂	0.96	Pos	20
	Meta	10	-CHO	-I	0.46	Pos	20
	Ortho	10	-NO ₂	-NH ₂	1.71	Pos	20
H ₃ ¹³ C-	Para	10	-CN	-F	1.0	Pos	21
	Meta	8	-F	-OH	1.9	Neg	21
	Ortho	7	-Br	-F	8.1	Pos	21
(CH ₃) ₃ ¹³ C-	Para	8	-NO ₂	-N(CH ₃) ₂	1.61	Pos	22
H ₂ ¹⁴ N-	Para	8	-NO ₂	-NH ₂	23.6	Pos	23
	Meta	6	-NO ₂	-CH ₃	4.5	Pos	23
H ₂ ¹⁵ N-	Para	8	-NO ₂	-OCH ₃	25.5	Pos	24
	Meta	8	-NO ₂	-CH ₃	5.7	Pos	24
O ₂ ¹⁴ N-	Para	6	-NO ₂	-NH ₂	5.5	Neg	25, 26
	Meta	6	-NO ₂	-OCH ₃	5.0	Neg	25
	Ortho	6	-NO ₂	-OCH ₃	6.0	Neg	25
O ₂ ¹⁵ N-	Para	9	-NO ₂	-NH ₂	8.23	Pos	27
¹⁹ F-	Para	14	-NO ₂	-NH ₂	25.4	Pos	28
	Meta	14	-NO ₂	-CH ₃	4.2	Pos	28
	Ortho	14	-Br	-F	31.4	Neg	28
(CH ₃) ₃ ²⁹ Si-	Para	6	-NO ₂	-OCH ₃	2.43	Pos	29
	Meta	4	-NO ₂	-CH ₃	2.26	Pos	29
	Ortho	3	-NO ₂	-CH ₃	3.42	Pos	29
F ₃ ²⁹ Si-	Para	6	-CF ₃	-OCH ₃	2.83	Neg	30
	Meta	6	-CF ₃	-CH ₃	1.74	Neg	30
(HO) ₂ ³¹ P=O	Para	12	-NO ₂	-OH	6.05	Neg	31
	Meta	9	-NO ₂	-OH	5.06	Neg	31
HO- ³¹ P(=O) ₂	Para	11	-NO ₂	-NH ₂	3.50	Neg	31
	Meta	8	-NO ₂	-OH	4.32	Neg	31
(CH ₃) ₃ ¹¹⁹ Sn-	Para	10	-Br	- <i>t</i> -Bu	5.57	Pos	<i>e</i>
	Meta	6	-CF ₃	-H	6.45	Pos	<i>e</i>
	Ortho	10	-CF ₃	-N(CH ₃) ₂	33.8	Pos	<i>e</i>
Cl ¹⁹⁹ Hg-	Para	7	-CF ₃	-CH ₃	106	Neg	8, 9
(CH ₃) ₃ ²⁰⁷ Pb-	Para	6	-F	-H	13.5	Neg	8, 9
	Meta	6	-CF ₃ , -Cl	-H	15.0	Neg	8, 9

^a Number of compounds studied in each category. ^b The substituent group producing the limiting shift at each end of the range, arranged under more positive and more negative Hammett σ values. Para constants were used to list the ortho substituents for which no constants are available. ^c The total chemical shift range in ppm. ^d A positive trend is defined as one in which electron withdrawal generally gives rise to a downfield shift (deshielding). ^e This work.

negatively,^{8,9} while tin responds as expected in the closely related phenyltrimethylmetal derivatives. In addition, the phosphorus-31 shifts in substituted phenylphosphonic acid anions, in which the phosphorus atom has a higher total charge, fail to reverse the inverse correlation found for the neutral acid molecules.³¹ No satisfactory theoretical basis is available to rationalize these data.

For the tin chemical shifts there is apparently good internal consistency; while only poor results are obtained when the meta and para data are plotted against their respective Hammett σ constants, excellent correlations are found when data for each category of substituent group are plotted against σ_I and σ_R° values.¹⁹ The correlation coefficients, r , are in each case >0.97 as shown in Table IV. Correlations against corresponding NMR data for other nuclei vs. $\delta^{119}\text{Sn}$ were also tested, but very poor coefficients were found for plots vs. proton,²⁰ carbon-13^{21,22} and mercury-199^{8,9} data. The tin-119 shifts did, however, correlate inversely with the shifts of lead-207 in substituted phenyltrimethyllead compounds^{8,9} ($r = 0.89$; $n = 11$) and especially well with the data for the para derivatives^{8,9} ($r = 0.96$; $n = 6$).

The σ_I and σ_R° scale is based upon a combination of rate, equilibria, and fluorine-19 NMR shift data for substituted benzenes in which d orbitals play no part. The correlations between these substituent constants and the tin-119 shieldings in the substituted phenyltrimethyltins suggest that d orbital effects are not important in determining the

chemical shift variations in these series, and similar conclusions have been drawn for the substituted phenyltrimethylsilanes on the basis of silicon-29 NMR shift data.²⁹

Unlike the silicon case, the tin shift values for the ortho and para derivatives are generally very different, ranging from the halogen values which are most similar ($\Delta\delta = +1.4$ (Cl), and -2.6 ppm (F)) and increase to a difference of $+16.3$ ppm for the dimethylamino group. In addition, the ortho chlorine resonance lies downfield of the para, while all the others lie upfield.

The shielding of ortho nuclei cannot generally be explained in terms of inductive and resonance effects alone, and it is thought that the shielding is appreciably influenced by diamagnetic anisotropy effects in the case of the proton but that the magnitude of such influences would be relatively the same for any nucleus and hence could not account for the larger shifts seen in the heavier spin nuclei.^{8,33} For the nonprotonic spectra, two effects have been discussed. A deshielding due to intramolecular electric fields or dispersion forces has been observed in the fluorine-19 spectra of chloro-substituted perfluorobenzenes.³⁴ On the other hand the chemical shifts of sterically perturbed carbon atoms are generally found at higher fields than for similar carbons not spatially crowded.³⁵ In our previous study³ we found that the presence of adjacent polarizable groups and atoms gave rise to upfield tin chemical shifts, and the range of compounds available here allows a more detailed examination of this factor.

Table VII. Tin-119 Chemical Shifts of Di- and Trimethyltin Derivatives (25% v/v in CH₂Cl₂) ±0.2 ppm

No. ^a	Compound	δ (¹¹⁹ Sn) ^b
1	(CH ₃) ₃ SnCH(CH ₃) ₂	+8.6 ^c
2	(CH ₃) ₃ SnCH ₂ CH ₃	+4.2 ^d
3	(CH ₃) ₃ SnCH ₂ CH ₂ CH ₂ CH ₃	-1.0 ^e
4	(CH ₃) ₃ SnCH ₂ CH ₂ CH ₃	-2.3 ^f
5	(CH ₃) ₃ SnCH ₂ C(CH ₃) ₃	-14.2
6	(CH ₃) ₃ Sn-c-C ₆ H ₅	+14.0
7	(CH ₃) ₃ Sn-c-C ₆ H ₁₁	-4.7 ^g
8	(CH ₃) ₃ Sn(adamantane-1)	-6.9
9	(CH ₃) ₃ Sn(adamantane-2)	-13.7
10	(CH ₃) ₃ Sn(norbornane-1)	+4.4
11	(CH ₃) ₃ Sn(norbornane-7)	-9.2
12	(CH ₃) ₃ Sn(<i>syn</i> -norbornene-7)	-11.3
13	(CH ₃) ₃ Sn(<i>anti</i> -norbornene-7)	-25.6
14	1-(CH ₃) ₃ Sn(dimethylallene-1,3)	-13.8
15	(CH ₃) ₃ Sn(naphthylene-1)	-31.8
16	1-(CH ₃) ₃ Sn(<i>n</i> -butylacetylene-2)	-72.0

^a Listed in order of increasing upfield shift within categories. ^b A negative sign indicates a resonance upfield of tetramethyltin. ^c Listed as +9.9 ppm as the neat liquid in ref 7. ^d Listed as +3.0 ± 0.1 in CCl₄ in ref 6, as +3.0 (0.5) in 30% C₆H₆ in ref 5, and as +5.9 as the neat liquid in ref 7. ^e Listed as -2 ± 0.3 ppm in 10% C₆H₆ in ref 6. ^f Listed as -2.9 ppm as the neat liquid in ref 7. ^g Listed as -5.0 ± 0.5 in 10% CH₂Cl₂ in ref 6 and as -1.7 ppm as the neat liquid in ref 7.

The trends revealed for the para to ortho shift are confirmed by extension to the 2,6-derivatives. Converting the ortho to the 2,6-dichloro derivative drives the tin shift still more downfield, and the perchloro compound is found farther downfield still. The shifts of the fluoro derivatives, whether para, meta, ortho, or 2,6-disubstituted, remain relatively constant, while the tin resonances of the methyl, methoxy, and ethoxy compounds shift farther upfield on 2,6-disubstitution. Like the chlorine case, substitution by the -CF₃ group (where no para derivative was available) moves the tin shift successively downfield in the sequence meta > ortho > 2,6-disubstituted. Thus those substituents containing alkyl groups give rise to upfield shifts when placed in ortho or 2,6-positions to tin. The methyl group data are instructive in this regard: para = meta (29.92) < ortho = 2,3- = 2,4- (34.0) < 2,6-disubstituted = 2,4,6-trisubstituted (50 ppm). Clearly, two different mechanisms are operating here. The upfield shifts can arise from sterically induced charge polarizations which increase charge densities at the crowded tin atom,³⁵ while dispersion forces may account for the downfield shifts in the halo derivatives.³⁴

An additional direct interaction across space to the tin atom is possible for the fluoro, chloro, and trifluoromethyl substituents which possess lone pair electrons, however. One measure of such interaction would be through the tin-119m Mössbauer quadrupole splitting (QS) which would be expected to be sensitive to the electric field gradient created in such a resulting higher coordinated species.³⁶ Indeed, as shown in Table V, the *o*-CF₃ derivative does exhibit a small QS, and the large line width of the *o*-fluoro derivative is suggestive of an incipient splitting. Moreover, all three substituents exhibit doublet spectra when attached at the 2,6-positions.

However, the *p*-fluoro and -chloro derivatives also exhibit large line width spectra, and such high coordination at tin would be expected to give rise to large, upfield shifts such as those found for other higher coordinated species.^{3,4} The observed tin-fluorine coupling to the *o*-fluoro and trifluoromethyl substituents can be compared to the values obtained for the analogous couplings to the *m*-CF₃, *m*- and *p*-fluorine atoms, and to the coupling to the α -fluorine atoms in the perfluoroethyltin system ($^2J(^{119}\text{Sn}-\text{C}-^{19}\text{F}) \approx 300$ Hz).³ In this case the tin-fluorine internuclear distance

should be ca. 2.9 Å, making reasonable assumptions, while the distance between tin and an *o*-fluoro atom is ca. 3.2 Å, outside the sum of the van der Waals radii (ca. 3.0 Å). Most likely the Mössbauer QS arises from electronegativity differences.³ A study of $|J(^{119}\text{Sn}-^{19}\text{F})|$ and ¹¹⁹Sn chemical shifts in a series of trifluoromethyltin derivatives which appeared while this paper was being processed corroborates our finding of lack of higher coordination at the tin atom in these systems.³⁷

The ortho substituent in our substituted phenyltrimethyltins occupies a position which is formally γ to the tin atom. It is now generally accepted that the upfield shift seen in carbon-13 resonances substituted at the γ position is produced by perturbation of the C-H bonds at the γ -carbon by steric interference with the substituent. Substitution at the α - and β -positions produces a downfield shift.³⁸ Similar α -, β -, and γ -effects have been observed for boron-11 shifts in amino-boranes,³⁹ nitrogen-14 shifts in trialkylamines, tetraalkylammonium ions, and nitroalkanes,⁴⁰ nitrogen-15 shifts in amines and hydrazines,⁴¹ silicon-29 shifts in tetraalkylsilanes,²⁹ and phosphorus-31 shifts in trialkylphosphoryl compounds.⁴²

The chemical shifts of 15 tetraorganotin derivatives are listed in Table VII. The shifts recorded thus far for the tetraalkyl series span a range of 57.9 ppm between that for tetraisopropyltin (-43.9 ppm)⁷ and trimethylcyclopropyltin (+14.0 ppm). By comparing suitably chosen pairs of data it is possible to estimate the effect of substituting a saturated carbon atom for a hydrogen at positions α , β , and γ to tin. Confining attention to the trimethyltin compounds, which have been most studied, $\Delta\delta_\alpha(\text{Me}_3\text{SnH} \rightarrow \text{Me}_3\text{SnCH}_3) = -104.5$; $\Delta\delta_\beta(\text{Me}_3\text{SnCH}_3 \rightarrow \text{Me}_3\text{SnCH}_2\text{CH}_3) \approx -5$; and $\Delta\delta_\gamma(\text{Me}_3\text{SnCH}_2\text{CH}_3 \rightarrow \text{Me}_3\text{SnCH}_2\text{CH}_2\text{CH}_3) \approx +6.5$ ppm. Thus the tin chemical shift apparently behaves, at least so far as the limited trimethyltin data available suggest, in a manner similar to that for carbon-13³⁸ and heavier nuclei,^{29,39-42} namely that α - and β -substitution produces a downfield shift, while γ -substitution gives rise to an upfield shift. The additivity of $\Delta\delta_\beta$ can be illustrated by the series $\text{Me}_3\text{SnCH}_2\text{CH}_3$ (-4.2), $\text{Me}_3\text{SnCH}(\text{CH}_3)_2$ (-8.6), and $\text{Me}_3\text{SnC}(\text{CH}_3)_3$ (-17.5 ppm)⁷, and of $\Delta\delta_\gamma$ by the compounds $\text{Me}_3\text{SnCH}_2\text{CH}_2\text{CH}_3$ (+6.6) and $\text{Me}_3\text{SnCH}_2\text{C}(\text{CH}_3)_3$ (+18.2 ppm). The similarity in the sign of the α -, β -, and γ -effects arising from the presence of a saturated carbon atom in the six nuclei ¹³C, ¹¹B, ¹⁴N, ¹⁵N, ²⁹Si, and ³¹P suggests a similar mechanism governing the shifts in each case.

The factors influencing this effect have been discussed by Roberts et al. in connection with a study of carbon-13 shifts in substituted norboranes.⁴³ In that study the 1-methyl group resonance was found to be downfield by 3.4 ppm of the 7-methyl resonance in 1,7,7-trimethylnorbornane. We find that the tin-119 resonance of the trimethylstannyl group in the 1-position is likewise downfield (by 13.6 ppm) of the 7-isomer as shown in Table VII. More interesting, and curious, is the situation with regard to syn and anti substitution in the 7-trimethylstannylnorbornenes. The two 7-methyl resonances differ by only 0.2 ppm (syn more shielded) in the 1,7,7-trimethylnorbornenes,⁴³ but the 7-*syn*-trimethylstannyl derivative lies downfield by 14.3 ppm from its anti isomer. However, the syn isomer is found only 2.2 ppm upfield from the saturated 7-trimethylstannylnorbornane. Additional derivatives must be examined before it can be decided whether the proximity of the unsaturated center produces little change, as the norbornane-norbornene comparison would suggest, or a large downfield shift as the syn-anti comparison would suggest. From the open-chain analogs, $\text{Me}_3\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (-1.00) and $\text{Me}_3\text{SnCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (-0.5 ppm)⁴⁴ the former view is

probably correct, but the large upfield shift seen in the anti isomer would then go unexplained.

Incorporation of a dimethyltin fragment into a carbon ring decreases the shielding with respect to tetramethylstannane as shown in Table VII, but the comparison with the open-chain analogs is more instructive: $\text{Me}_2\text{Sn}(\text{CH}_2)_6$ (+4.5) vs. Me_2SnEt_2 or $n\text{-Pr}_2$ (-2 ppm),⁶ $\text{Me}_2\text{Sn}(\text{CH}_2)_4$ (+55.1) vs. Me_2SnEt_2 (+7 ppm),⁴⁵ the stannole $\text{Me}_2\text{Sn}(\text{C}_6\text{H}_5)_4$ (-52)³ vs. $\text{Me}_2\text{Sn}(\text{CH}=\text{CH}_2)_2$ (+79.4 ppm).⁷ Incorporation into a seven-membered stannacycloheptane apparently has little effect, but the strain induced in the five-membered stannacyclopentane gives rise to a large downfield shift, and an even larger shift is experienced on ring closure of the divinyl system to the unsaturated stannole.

Substitution of unsaturated for saturated groups generally leads to shifts to higher fields as in the trimethyltin vinyl (-35.4,⁷ -40⁸) and acetylene derivatives ($\text{Me}_3\text{Sn}-\text{C}\equiv\text{CC}_6\text{H}_5$ (-69),³ $\text{Me}_3\text{SnC}\equiv\text{C}(\text{CH}_2)_3\text{CH}_3$ (-72.0)) and in the phenyl (-30.3) and 1-naphthyl (-31.8 ppm) derivatives. Separation by a methylene group insulates the tin atom from the effect as in $\text{Me}_3\text{SnCH}_2\text{CH}=\text{CH}_2$ (-0.5),⁴⁵ and $\text{Me}_3\text{SnCH}_2\text{C}_6\text{H}_5$ (+4 ppm),³ whose shifts are close to those of saturated analogs. Attachment to cyclopentadienyl (+23.3)¹⁰ or indenyl (+31.3 ppm)¹⁰ rings brings about large downfield shifts, however. The shift of the allyl (-13.8 ppm) derivative falls lowest among the directly attached, acyclic unsaturated substituents studied.

Experimental Section

NMR Parameters. Natural abundance tin-119 NMR chemical shifts were measured at 37.27 MHz by direct observation in the continuous wave mode on a Varian XL-100-15 spectrometer. Samples were contained in 10-mm tubes, which were held concentrically inside 12-mm tubes with the outer annulus containing acetone-*d*₆, the field/frequency lock material. Broad band proton noise decoupling was provided by the Gyrocode matrix of the XL-100. Chemical shifts are relative to external tetramethyltin. Measurements were not corrected for bulk magnetic susceptibility differences, which were estimated to be less than the experimental error. Values are averages of at least five traces in both directions at a sweep width of 500 Hz and sweep time of 100 sec and are believed accurate to ± 0.2 ppm. Solution concentrations were 50% (vol/vol for liquids or wt/vol for solids) in spectroquality grade CCl_4 for substituted aryltrimethyltins and 25% in CH_2Cl_2 for the tetraalkyltins. Ambient probe temperature was 39°.

Compounds. Substituted aryltrimethyltin derivatives were obtained by reaction of trimethyltin chloride with the appropriate organolithium (L) or Grignard reagent (G) in anhydrous THF or diethyl ether (both distilled from CaH_2) under an atmosphere of argon, followed by hydrolysis with saturated aqueous ammonium chloride solution, extraction of the aqueous phase, and vacuum distillation. In several cases, distilled products were purified further on an F & M Model 775 preparative gas chromatograph, operating in the isothermal mode. An 8 ft., $\frac{3}{4}$ in. i.d., Apiezon-L (10%) on Chromosorb P column was used, with a helium flow rate of ca. 0.5 l./min. Purity of all compounds probably exceeded 95%, as indicated by absence of spurious signals in the proton magnetic resonance spectra. Method of preparation, boiling points, and melting points are as follows: *o*- OCH_3 (G), bp 103-103.5° (5 mm) (lit.⁴⁶ bp 70° (1.2 mm)); *o*- CH_3 (G), bp 100-100.5° (9 mm) (lit.⁴⁶ bp 90° (7 mm)); *o*-Cl (G), bp 99-101° (5 mm) (lit.⁴⁷ bp 47° (0.5 mm)); *o*- CF_3 (G), bp 64.5° (3 mm) (lit.⁴⁶ bp 67° (3.6 mm)); *o*-F (L), bp 86° (11 mm) (lit. bp 65° (4 mm)),⁴⁸ 63-64° (7 mm⁴⁹); *p*-*r*-(C_4H_9) (G), mp 71.5-72° (lit.⁴⁶ mp 74°); 3,5-(CF_3)₂ (G), bp 85-86° (10 mm) (lit.⁴⁶ bp 81-82° (8.5 mm)); 2,4-(CH_3)₂ (G), bp 111° (7 mm) (lit.⁴⁶ bp 84° (2.5 mm)); 1-trimethyltinnaphthalene (G), bp 114° (0.75 mm) (lit.⁵⁰ bp 120-121° (1 mm)).

o-Ethoxyphenyltrimethyltin was obtained in 80% yield from the Grignard reagent of *o*-bromophenetole and trimethyltin chloride in THF (bp 111.5-113° (5.5 mm)). Anal. Found: C, 46.70; H, 6.43. $\text{C}_{11}\text{H}_{18}\text{OSn}$ Calcd: C, 46.36; H, 6.32.

o-*N,N*-Dimethylaminophenyltrimethyltin was produced in 77%

yield from the reaction of commercial *n*-butyllithium (15.1% in *n*-hexane) with *o*-bromo-*N,N*-dimethylaniline in diethyl ether, followed by addition of trimethyltin chloride in ether (bp 76-77° (0.5 mm)). Anal. Found: C, 46.59; H, 6.76. $\text{C}_{11}\text{H}_{19}\text{NSn}$ Calcd: C, 46.52; H, 6.74.

o-Ethylphenyltrimethyltin was prepared in 70% yield from the Grignard reagent of *o*-bromoethylbenzene and trimethyltin chloride in THF (bp 68-69° (0.75 mm)). Anal. Found: C, 49.06; H, 6.73. $\text{C}_{11}\text{H}_{18}\text{Sn}$ Calcd: C, 49.12; H, 6.74.

2,6-Dimethoxyphenyltrimethyltin was synthesized in 80% yield from the metalation of 1,3-dimethoxybenzene⁵¹⁻⁵³ by *n*-butyllithium, followed by treatment with a solution of trimethyltin chloride in ether. An analytically pure sample was obtained by preparative gas chromatography (bp 110-111° (3 mm), mp 36-37.5°). Anal. Found: C, 44.18; H, 6.12. $\text{C}_{11}\text{H}_{18}\text{O}_2\text{Sn}$ Calcd: C, 43.90; H, 6.03.

2,6-Diethoxyphenyltrimethyltin was obtained in 73% yield from *n*-butyllithium and 1,3-diethoxybenzene (RSA Corp., Ardsley, N.Y.) in THF, followed by trimethyltin chloride in THF (mp 78-78.5°). Anal. Found: C, 47.53; H, 6.71. $\text{C}_{13}\text{H}_{22}\text{O}_2\text{Sn}$ Calcd: C, 47.46; H, 6.69.

2,6-Dimethylphenyltrimethyltin was produced in 83% yield from the Grignard reagent of 2-bromo-*m*-xylene in diethyl ether, followed by reaction with trimethyltin chloride in ether (bp 121.5° (10 mm)). Anal. Found: C, 49.21; H, 6.75. $\text{C}_{11}\text{H}_{18}\text{Sn}$ Calcd: C, 49.12; H, 6.74.

2,6-Bis(trifluoromethyl)phenyltrimethyltin was prepared in 30% yield by metalation of 1,3-bis(trifluoromethyl)benzene (Pierce Chemical Co., Rockford, Ill.) in THF with *n*-butyllithium, followed by treatment with a solution of trimethyltin chloride in THF. The 2,6-derivative was separated from the 2,4-isomer⁵⁴ (ca. 60/40 mixture of 2,4- and 2,6-bis(trifluoromethyl)phenyltrimethyltins) by preparative gas chromatography (bp 90-94° (10-11 mm)). Anal. Found: C, 35.31; H, 3.30. $\text{C}_{11}\text{H}_{12}\text{F}_6\text{Sn}$ Calcd: C, 35.05; H, 3.20.

2,4-Bis(trifluoromethyl)phenyltrimethyltin was isolated from the mixture of isomers produced in the preparation of the 2,6-derivative (*vide supra*) by preparative gas chromatography (bp 90-94° (10-11 mm)). Anal. Found: C, 34.51; H, 3.19. $\text{C}_{11}\text{H}_{12}\text{F}_6\text{Sn}$ Calcd: C, 35.05; H, 3.20.

2,6-Difluorophenyltrimethyltin was obtained in 60% yield by metalation of 1,3-difluorobenzene in THF with *n*-butyllithium⁵⁸ at -78°,⁵⁹ followed by addition of trimethyltin chloride in THF. Purification by preparative gas chromatography yielded a single isomer (bp 80° (9 mm)). Anal. Found: C, 38.67; H, 4.53. $\text{C}_9\text{H}_{12}\text{F}_2\text{Sn}$ Calcd: C, 39.04; H, 4.36.

3,4-Dimethylphenyltrimethyltin was synthesized in 75% yield from the Grignard reagent of 4-bromo-*o*-xylene in THF, followed by addition of a trimethyltin chloride solution in THF (bp 108° (6 mm)). Anal. Found: C, 49.04; H, 6.83. $\text{C}_{11}\text{H}_{18}\text{Sn}$ Calcd: C, 49.12; H, 6.74.

2,4,6-Trimethoxyphenyltrimethyltin was prepared by metalation of 1,3,5-trimethoxybenzene in THF with *n*-butyllithium, followed by addition of trimethyltin chloride in THF (bp 131° (1.0 mm); mp 56-58°). Anal. Found: C, 43.69; H, 6.22. $\text{C}_{12}\text{H}_{20}\text{O}_3\text{Sn}$ Calcd: C, 43.54; H, 6.09.

Additional meta- and para-substituted aryltrimethyltins¹ and aliphatic derivatives⁶²⁻⁶⁴ were available from previous investigations.

Mössbauer Parameters. Our cam-drive, constant-acceleration Mössbauer spectrometer and curve fitting procedures have been described in detail.⁶⁵ Mössbauer spectra were calibrated against an NBS 5 mil β -tin foil as having an absolute value of 2.56 mm/sec (lit.⁶⁶ 2.56 \pm 0.01 mm/sec). SnTe which has been suggested as an isomer shift standard for tin⁶⁷ has a value of 3.43 \pm 0.06 mm/sec (lit.⁶⁵ 3.43 \pm 0.02 mm/sec) on this basis.

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methyltin derivatives, and the regression analysis data were computed by Mr. F. Sheffy of Franklin and Marshall College.

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