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PULSED FOURIER TRANSFORM NMR OF SUBSTITUTED ARYLTRIMETHYLTIN DERIVATIVES

II. (^{119}Sn–^{13}C) COUPLING CONSTANTS AND ^{13}C CHEMICAL SHIFTS OF *meta*- AND *para*-DERIVATIVES*

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SUMMARY

Carbon-13 NMR data are reported for thirteen *para*- and *meta*-substituted phenyltrimethyltin compounds, $RC_6H_4Sn(CH_3)_3$, where R = *para*-$N(CH_3)_2$, *para*-OCH_3, *para*-OC_2H_5, *para*-CH_3, *meta*-CH_3, -H, *para*-F, *meta*-OCH_3, *para*-Cl, *para*-Br, *meta*-F, *meta*-Cl and *para*-$Sn(CH_3)_3$. In the *para*-derivatives, correlation coefficients with Hammett σ-constants of greater than ca. 0.9 are obtained with the tin–carbon couplings to methyl, C_1 and C_4 carbons, and with the carbon-13 chemical shifts $\delta(C(1))$. In the *meta*-derivatives, the couplings $|J(Sn–CH_3)|$, $|J(Sn–C(1))|$, $|J(Sn–C(3))|$ and $|J(Sn–C(6))|$, and the shifts $\delta(C(1))$ and $\delta(C(5))$ correlate well with Hammett σ. In the *para*-derivatives, sensitivity to change in substituent falls off $C(4) > C(3,5) > C(1) > C(2,6) > CH_3$ as registered by the $\delta(C)$, while in the *meta*-derivatives $\delta(C)$ changes decrease $C(3) > C(2)$, $C(4) > C(1) > C(5)$, $C(6) > CH_3$. The magnitudes of the tin coupling constants decrease $C(1) > CH_3 > C(3,5) > C(2,6) > C(4)$ in the *para*-derivatives, while in the *meta*-series the order is $C(1) > CH_3 > C(3)$, $C(5) > C(2) > C(6) > C(4)$. The two sets of one-bond $|J(Sn–CH_3)|$ and $|J(Sn–C(1)|$ values correspond closely to the 0.25/0.33 ratio of coefficients in the LCAO approach, and are interpreted in terms of *s*-electron redistributions at the tin atom with change in substituent.

INTRODUCTION

There has been much interest in the carbon-13 NMR parameters of substituted fluorobenzenes, since unequivocal assignments of the ring carbon atoms are more easily obtained owing to the couplings produced by the spin of one half nucleus of fluorine. In addition, the carbon–fluorine coupling constants combine with the carbon-13 and fluorine-19 chemical shift data to give a comprehensive picture of the electron distributions in these molecules[2–6]. We have extended these studies to a series which possesses many of the same advantages, the substituted phenyltrimethyltin

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compounds, in which the two spin of one half nuclei, tin-117 and tin-119, serve to label the various ring carbon atoms with characteristic doublet satellite patterns as an aid to assignment. Moreover, the tin atom, lacking the fluorine atom's lone pair electrons and extreme electronegativity, is expected to produce a far different effect than is seen in the fluorobenzenes, and as such to provide a useful comparison with that series. In addition, the trimethyltin group, unlike the fluorine atom, provides another probe into the molecule through the methyl carbon chemical shift and coupling data. We report in this paper carbon-13 NMR data for thirteen *meta-* and *para*-substituted aryltrimethyltin compounds.

EXPERIMENTAL

Compounds

Substituted aryltrimethyltins were obtained by reaction of trimethyltin chloride with the appropriate organolithium (L) or Grignard reagent (G) in anhydrous diethyl ether (distilled from CaH_2) under an atmosphere of argon, followed by hydrolysis with saturated aqueous ammonium chloride solution, ether extraction, and vacuum distillation. In several cases, highest boiling fractions were distilled further on an annular spinning band distillation column. Purity of all compounds probably exceeded 95%, as indicated by absence of spurious signals in the proton magnetic resonance (PMR) spectra. Method of preparation, boiling points, and melting points are as follows: *p*-Cl (G), b.p. 115°/11 mm (lit. b.p. 80°/2.3 mm[8], 122–126°/22 mm[9], 82–85°/ca. 2 mm[10]); *p*-Br (G), b.p. 129–130°/9.5 mm (lit. b.p. 124°/15 mm[11], 89–90°/1 mm[10], 85.5–86.5°/0.5 mm[12]); *m*-Cl (G), b.p. 112°/9.5 mm (lit.[8] b.p. 96°/3.5 mm); *p*-F (G), b.p. 88°/12 mm (lit. b.p. 88°/10 mm[10], 50–51°/0.7–0.8 mm[13], 88°/11 mm[14]); *m*-F (G), b.p. 89–90°/11 mm (lit. b.p. 55–57°/1.8–2.4 mm[13], 83°/9 mm[14]); *p*-CH_3 (G), b.p. 109°/14 mm (lit. b.p. 224.4°/760 mm[12], 80.5°/3 mm[8], 100°/6 mm[10]); *m*-CH_3 (G), b.p. 104°/11 mm (lit.[12] b.p. 65.5–67°/0.6 mm); *p*-OCH_3 (G), b.p. 128°/14 mm (lit. b.p. 125–127°/15 mm[12], 100–102°/10–12 mm[10]); *m*-OCH_3 (G), b.p. 123–124°/12 mm (lit.[15] b.p. 61°/0.4 mm); *p*-$N(CH_3)_2$ (L), b.p. 151°/10 mm, m.p. 39.5–41° (lit. b.p. 102–104°/6 mm, m.p. 40–41° [10], b.p. 97°/0.85 mm, m.p. 38° [8]); *p*-$Sn(CH_3)_3$ (G), m.p. 123–125° (lit. m.p. 123–124° [16], 124–125° [12], 123–125° [9], 122–124° [17]); H (G), b.p. 98°/20 mm (lit. b.p. 203–208°/760 mm[18], 205–206°/760 mm[10], 76.5°/0.9 mm[19], 50–53°/0.2 mm[17]).

p-Ethoxyphenyltrimethyltin was prepared in 60% yield by reaction of *p*-bromophenetole (9.9 g, 0.049 mol) with Mg turnings (1.4 g, 0.058 mol) in anhydrous diethyl ether, followed by addition of trimethyltin chloride (9.8 g, 0.049 mol) in ether. The reaction mixture was refluxed for 2 h, and then was hydrolyzed with saturated aqueous ammonium chloride solution. After ether extraction, the combined extracts were dried over magnesium sulfate. Ether was removed under vacuum and the resulting pale yellow liquid was fractionated under reduced pressure on a 12-inch jacketed column packed with glass helices (b.p. 133.5–134°/10 mm) Anal.* Found: C, 46.51; H, 6.28; Sn, 40.24%. $C_{11}H_{18}OSn$ calcd.: C, 46.36; H, 6.32; Sn, 41.69%.

NMR parameters

Natural abundance, proton noise-decoupled ^{13}C spectra were recorded at

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* Carbon, hydrogen analysis was performed by Instranal Laboratory, Inc., Rensselaer, N.Y. 12144. Tin analysis was performed gravimetrically in this laboratory by oxidization to SnO_2.

25.1 MHz on a modified Varian HA-100D NMR spectrometer equipped for continuous wave (cw), frequency sweep, fast Fourier transform (FFT) and ^{19}F lock operation. Data were collected and processed by a Digilab FTS/NMR-3 pulse and data system. Samples were contained in 8 mm O.D. tubes which held 2 mm O.D. coaxial inner cells filled with C_6F_6, the ^{19}F lock compound. Probe temperature was maintained at ca. 40° during proton-decoupled experiments utilizing the Digilab 50–80 decoupler by a continuous flow of nitrogen circulated through cooling coils held in Dry Ice.

Coupling constants were either read directly from Teletype print-out, or measured from calibrated chart paper. In all cases, 16384 (16K) data points were collected with a sampling frequency of 4000 s^{-1}, yielding a resolution of ca. ±0.25 Hz. The number of pulses ranged from 500 to 10000.

Carbon chemical shifts were measured in parts per million (ppm) relative to internal tetramethylsilane (TMS). Positive values are to high frequency. A resolution of ±0.03 ppm was achieved using 16K data points and sampling frequency of 12500 s^{-1}. Normally, 100 pulses were collected for each compound. Carbon chemical shifts of ring carbons were also measured in ppm relative to 10% (vol/vol) internal benzene. The assigned error is ±0.02 ppm.

RESULTS

The carbon-13 chemical shifts are listed in ppm from internal TMS (±0.03 ppm) in Table 1. Assignments of the aromatic carbon resonances are based upon additivity relationships[3,4,7,20–22] (see Table 2), and confirmed by observations from undecoupled spectra, and from tin–carbon coupling information listed in Table 3. Table 2 compares the chemical shifts, relative to internal benzene, found in this study with those obtained assuming additivity. The two sets of data are in reasonably good qualitative agreement, and it appears that peak assignments based upon the additivity

TABLE 1

CARBON-13 CHEMICAL SHIFTS IN ppm FROM INTERNAL TMS (±0.03 ppm)[a]

Compound	*C*(1)	*C*(2)	*C*(3)	*C*(4)	*C*(5)	*C*(6)	*CH*$_3$
p-$N(CH_3)_2$[b]	126.02	136.25	112.76	150.52	112.76	136.25	−9.58
p-OCH_3	131.68	136.70	114.29	160.27	114.29	136.70	−9.64
p-OC_2H_5	131.49	136.67	114.92	159.62	114.92	136.67	−9.64
p-CH_3	137.58	135.64	128.97	137.29	128.97	135.64	−9.69
m-CH_3	141.23	136.31	136.80	128.98	127.96	132.72	−9.85
H	141.53	135.66	128.07	128.07	128.07	135.66	−9.77
p-F	136.88	137.38	115.68	168.51	115.68	137.38	−9.72
	136.72	137.11	114.94	158.68	114.94	137.11	
m-OCH_3	142.90	121.53	159.49	113.61	129.00	127.91	−9.60
p-Cl	139.82	136.75	128.15	134.52	128.15	136.75	−9.64
p-Br	140.18	136.91	130.92	122.83	130.92	136.91	−9.58
m-F	144.88	122.41	167.90	115.54	129.63	131.27	−9.78
	144.77	121.71	157.95	114.70	129.83	131.16	
m-Cl	144.29	135.25	134.46	128.16	129.12	133.37	−9.66
p-$Sn(CH_3)_3$[c]	141.30	135.38	135.38	141.30	135.38	135.38	−9.82

[a] Neat liquids. [b] Liquid phase (ca. 50°). [c] Saturated solution in CCl_4.

TABLE 2

CARBON-13 CHEMICAL SHIFTS IN ppm FROM 10% INTERNAL BENZENE (±0.02 ppm)[a]

Compound		*C*(1)	*C*(2)	*C*(3)	*C*(4)	*C*(5)	*C*(6)
p-$N(CH_3)_2$	found	+ 0.7	+8.3	−15.3	+22.4	−15.3	+8.3
	calcd.[b]	+ 1.6	+8.4	−15.6	+22.5	−15.6	+8.4
p-OCH_3	found	+ 3.4	+8.5	−14.0	+32.0	−14.0	+8.5
	calcd.	+ 5.7	+8.5	−14.5	+31.3	−14.5	+8.5
p-OC_2H_5	found	+ 3.2	+8.4	−13.5	+31.3	−13.5	+8.4
	calcd.[c]	+ 5.5	+8.6	−13.8	+30.9	−13.8	+8.6
p-CH_3	found	+ 9.4	+7.5	+ 0.8	+ 9.2	+ 0.8	+7.5
	calcd.	+10.5	+7.4	+ 0.6	+ 8.8	+ 0.6	+7.4
m-CH_3	found	+13.1	+8.2	+ 8.7	+ 0.8	− 0.2	+4.6
	calcd.	+13.3	+8.2	+ 8.8	+ 0.6	− 0.2	+4.6
H	found	+13.4	+7.5	− 0.1	− 0.1	− 0.1	+7.5
p-F[d]	found	+ 8.5	+9.0	−13.0	+35.2	−13.0	+9.0
	calcd.	+ 8.9	+8.9	−13.0	+34.7	−13.0	+8.9
m-OCH_3	found	+14.7	−6.7	+31.2	−14.7	+ 0.8	−0.3
	calcd.	+14.4	−6.9	+31.3	−14.5	+ 0.9	−0.2
p-Cl	found	+11.7	+8.6	0.0	+ 6.4	0.0	+8.6
	calcd.	+11.5	+8.8	+ 0.3	+ 6.1	+ 0.3	+8.8
p-Br	found	+12.2	+9.0	+ 3.0	− 5.1	+ 3.0	+9.0
	calcd.	+11.8	+9.2	+ 3.3	− 5.6	+ 3.3	+9.2
m-F[d]	found	+16.6	−6.2	+34.6	−13.2	+ 1.2	+3.0
	calcd.	+14.8	−5.4	+34.7	−13.0	+ 1.3	+3.0
m-Cl	found	+16.2	+7.1	+ 6.3	+ 0.1	+ 1.1	+5.3
	calcd.	+14.7	+7.9	+ 6.1	+ 0.3	+ 1.2	+5.6
p-$Sn(CH_3)_3$	found	+13.2	+7.3	+ 7.3	+13.2	+ 7.3	+7.3
	calcd.	+13.3	+7.4	+ 7.4	+13.2	+ 7.4	+7.4

[a] Shifts to higher frequency are positive. Data for monosubstituted aromatics are from ref. 26. [b] Shifts for *N,N*-dimethylaniline were obtained from ref. 4. [c] Data for phenetole: *C*(1), +31.0; *C*(2, 6), −13.7; C(3, 5), +1.1; C(4), −7.9. [d] Average values of $J(^{13}C–^{19}F)$ used.

TABLE 3

$|(^{119}Sn–^{13}C)|$ COUPLING CONSTANTS (±0.25 Hz)[a]

Compound	*C*(1)	*C*(2)	*C*(3)	*C*(4)	*C*(5)	*C*(6)	*CH_3*
p-$N(CH_3)_2$[b]	520.2	42.0	51.8	10.0	51.8	42.0	343.6
p-OCH_3	493.2	42.3	51.7	11.0	51.7	42.3	348.0
p-OC_2H_5	496.7	42.2	51.8	11.0	51.8	42.2	347.2
p-CH_3	486.8	36.8	49.4	11.0	49.4	36.8	347.0
m-CH_3	480.4	36.2	47.5	11.0	50.5	35.7	346.2
H	474.4	36.6	47.4	10.8	47.4	36.6	347.5
p-F	467.0	48.6	70.0	11.8	70.0	48.6	353.0
	458.8	35.3	30.5	11.7	30.5	35.3	
m-OCH_3	471.0	41.1	59.3	10.2	54.6	35.3	347.5
p-Cl	454.1	39.4	48.1	12.2	48.1	39.4	352.8
p-Br	452.0	38.6	47.4	12.7	47.4	38.6	352.0
m-F	449.9	56.5	62.6	9.0	59.0	35.1	354.1
	445.0	54.7	62.5	8.6	46.4	29.8	
m-Cl	439.0	39.4	59.8	9.8	48.2	33.2	353.0
p-$Sn(CH_3)_3$[c]	477.0	34.2	44.6	9.8	44.6	34.2	347.5

[a] Neat liquids. [b] Measured in liquid phase (ca. 50°). [c] Saturated solution in CCl_4.

relationship may be made with confidence. Carbon chemical shifts of the unsubstituted, parent compound, phenyltrimethyltin, are consistent with those previously reported for the silicon homologue[4]. For *para*-substituted derivatives, four resonances are observed in the aromatic carbon region, with the two substituent-bearing carbons of considerably weaker intensity owing to low nuclear Overhauser enhancement[23]. The resonance position of C(1), the carbon atom bearing the trimethyltin function, generally appears upfield from C(4), the carbon atom carrying the substituent. In addition, the C(1) resonance is somewhat less sensitive to substituent variation than the C(4). For the *para*-chloro and *para*-bromo derivatives, however, the C(4) resonance appears upfield from C(1), owing to large shielding effects associated with these halogen atoms[22]. In all cases, large couplings (420–520 Hz) are observed between C(1) and tin, while markedly smaller couplings (10–13 Hz) are observed to C(4), as expected. Carbon resonances C(2) and C(6), *meta* to the substituent, are predictably less sensitive to substituent changes (range of shift ca. 2 ppm) than C(3) and C(5), which are *ortho* to the substituent. The C(3, 5) resonances invariably appear upfield from those of C(2, 6). The three-bond tin couplings to carbon atom C_3 and C_5 are, however, consistently larger in absolute magnitude than the two-bond couplings to C(2) and C(6), although no determination of relative signs was attempted*. Substituent groups containing

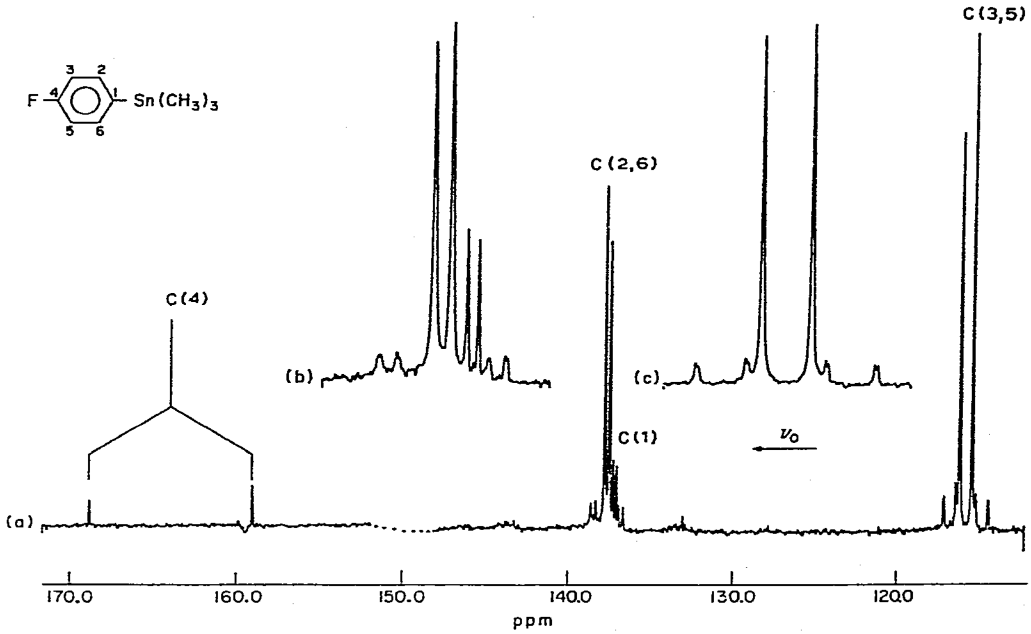

Fig. 1. (a) Aromatic carbons of *para*-fluorophenyltrimethyltin showing ^{13}C–^{19}F couplings (see Table 7). Scale is in ppm downfield from internal TMS. This proton noise-decoupled spectrum required 6000 pulses. using 16384 data points with a collection time of 4.1 s per pulse. The pulse width was 20 μs. Phase of sample: neat liquid. Dotted line at ca. 150 ppm indicates region of folded peak. (b) Region of C(2, 6) (left) and lower intensity C(1) carbon resonances. Conditions same as for (a), but region is four-fold expanded. (c) Region of C(3, 5) carbon resonance. Fluorine-split Sn–^{13}C satellites are clearly resolved into 117,119 components, as in (b). Conditions same as for (b).

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* $^1J(^{119}Sn$–$^{13}C)$ is believed to be opposite in sign to $^1J(^{13}C$–$^1H)$. See ref. 23.

highly electronegative atoms (F, O, N) bring about large downfield shifts in C(4) as expected[25].

The carbon-13 spectrum of *para*-fluorophenyltrimethyltin in the aromatic region is shown in Fig. 1.

The chemical shifts of the *meta*-substituted derivatives are assigned in a manner analogous to the *para*. Again, carbon C(1) displays the largest, and carbon C(4) the smallest coupling to tin, with couplings to carbons C(2) and C(6) (*ortho* to tin) once more considerably smaller than those to C(3) and C(5) (*meta* to tin). As expected, tin couplings to C(2) (*ortho* to both tin and the substituent) were rather sensitive to variations of substituent relative to those to C(6) (*ortho* to tin, but *meta* to the substituent) owing, presumably, to the proximity of C(2) and the substituent.

DISCUSSION

Chemical shifts

In the *para*-substituted fluorobenzene series there is a close correlation between the chemical shifts of the C(1) carbons and substituent constants, especially the Taft resonance parameters[4] which are themselves derived from ^{19}F chemical shift data for substituted fluorobenzenes[27]. Such correlations should be found only when both chemical reactivity, as represented by the substituent constants, and nuclear screening, as reflected in the chemical shifts, can be related to the electron density of the carbon atoms being examined. However, substituent constants derived from kinetic data have as their reference the transition state complex which may involve excited states of the reacting molecules as well as drastic polarizations brought about by the reacting groups. Nuclear screening, on the other hand, is affected by certain contributions which are purely magnetic in origin, as for example magnetic anisotropy and paramagnetic effects which have no direct bearing upon chemical behavior.

Examination of the regression analysis data for the correlation of the carbon-13 chemical shifts with the Hammett σ constants[28] in Table 4 reveals several notable trends. For the *para*-derivatives, as expected, the chemical shifts of the C(4) carbon which holds the substituent group are most affected by change in substituent, but the poor correlation coefficient suggests a rather complex interplay of factors, including inductive and resonance effects on the electronic environment of C(4), and other factors such as neighbor group anisotropy[20] and intramolecular dispersion interactions[29] which may be operative at the C(4) site. The *ortho*-carbon shifts (C(3, 5)) are next most sensitive to substituent group changes, but the scatter in the correlation is quite high, implying that extraneous factors are still important here. The best correlation is achieved for C(1) at which site inductive effects as well as dispersion, anisotropy and direct field effects should be negligible. The slope of the *ortho*-(C(3, 5)) and *para* (C(1) carbons is opposite to that of the carbon C(4) to which the substituent is directly attached. The *meta*-carbon (C(2, 6)) and methyltin carbon chemical shifts do not correlate with the Hammett σ-constant. Similar behavior is observed in the *para*-substituted bromobenzenes for C(1), C(4) and C(2, 6) carbons, but in this case the data for C(3, 5) (*ortho*) carbons fall into two groups depending upon the ability of the substituents to interact by resonance[22].

Turning to the correlation data for the *meta*-derivatives, in which all six carbon atoms of the ring are distinct, the methyltin carbons and one of the ring

TABLE 4

CARBON CHEMICAL SHIFT REGRESSION ANALYSIS PARAMETERS

	r^a	$\rho(ppm/\sigma)^b$	$C(ppm)^b$	n^c
Para-derivatives vs. σ				
C(1)	0.902	17.20	137.3	8
C(2,6)	0.332	0.68	136.5	8
C(3,5)	0.700	19.68	123.6	8
C(4)	0.522	−29.40	141.8	8
Methyl	0.245	− 0.06	−9.7	8
Meta-derivatives vs. σ				
C(1)	0.978	7.93	141.8	5
C(2)	0.373	−14.41	131.3	5
C(3)	0.388	30.90	139.7	5
C(4)	0.338	−13.19	124.8	5
C(5)	0.910	3.13	128.2	5
C(6)	0.178	− 2.59	132.6	5
Methyl	0.428	0.22	−9.8	5
All derivatives vs. σ				
C(1)	0.900	18.17	138.2	12
$C(x)^d$	0.249	−13.03	145.8	12
Methyl	0.202	− 0.06	−9.7	12

[a] Correlation coefficient. [b] Parameters of the equation $\delta=\rho\sigma+C$. [c] Number of compounds. [d] Substituent-bearing carbon atom (C(4) for *para* derivatives; C(3) for *meta* derivatives).

carbon atoms (C(5)) which is in a position *meta* to both the trimethyltin and substituent groups are again insensitive to change in substituent. Once more, the carbon atom bearing the substituent (C(3)) is most sensitive to change, but the correlation is poor. Next most sensitive is the site *ortho* to both the substituent and the trimethyltin group (C(2)), and the site *ortho* to the substituent alone (C(4)), but here again the correlation is poor. The methyltin and C(5) carbon atoms can be affected only by an inductive or direct field mechanism, which is negligible at these sites, while the C(3) and C(2), C(4) atoms are probably affected by several factors extraneous to chemical behavior. More surprising is the lack of sensitivity and poor correlation of the data for C(6), a site *para* to the substituent and *ortho* to the tin group, and the excellent correlation shown by the data for C(1) which is *meta* to the substituent. Combining data for all the compounds studied shows that the best correlation and greatest sensitivity is shown by the C(1) carbon atom. The observation of strong interaction with the C(1) carbon in the *meta*-substituted series cannot be rationalized on classical resonance arguments, since in these compounds C(1) is itself at a *meta*-site.

Coupling constants

Direct tin–carbon coupling constants have been recorded for only six methyltin compounds: $(CH_3)_4Sn$ (340±2[30], 336±3[31], 330±5[32]), $(CH_3)_3SnSn(CH_3)_3$ (240±0.5[33]), $(CH_3)_3SnBr$ (380±2[30], $(CH_3)_2SnCl_2$ (556±2[30]), CH_3SnBr_3 (640±15[30]) and $[(CH_3)_3Sn]_2C_5H_4$ (340±8[34]) and in tetraethyltin (321.5[35]) and tetraallyltin (250±3[34] Hz). The two-bond tin–carbon coupling constants in tetraethyltin (23.5[35]) and tetraallyltin (49.5±0.6) and $[(CH_3)_3Sn]_2C_5H_4$(9.6[34]) have been measured as have the three-bond couplings in tetraallyltin (50.6±0.6[34]) and $[(CH_3)_3Sn]_2C_5H_4$ (24.6[34] Hz).

Unlike the chemical shifts which reflect the situation at nuclear sites, the coupling constants are related in the Fermi contact mechanism to the product of the *s*-character of the orbitals forming the bonds intervening between the coupled nuclei. While the most satisfactory way to interpret substituent effects on the coupling constants would be to draw comparisons with values calculated from wave functions for each molecule, extended Hückel calculations using Pople–Santry formalism to evaluate the Fermi contact contribution to the coupling constants in substituted fluorobenzenes predicted only the one-bond couplings which the Pople–Santry recipe is specifically designed to reproduce, but failed to predict the longer-range values[5].

The tin coupling constant data in Table 3 are listed in order of increasing Hammett σ constant of the substituent group, except for the trimethyltin group data which are listed at the bottom of the Table. Substituent groups with negative σ constants are in general associated with lower absolute values of the couplings in the methyltin group than those with positive σ-constants, and there is a gradual, but not precisely monotonic, increase in the magnitudes of the couplings with increasing σ constant. The Table also lists phenyl group carbon–tin coupling constants. Data of this kind have not been reported before, and for the C(1) and the substituent-holding carbon are intrinsically more difficult to collect because of the absence of the signal-enhancing nuclear Overhauser effect with carbon atoms lacking a directly-bonded proton[23].

The regression analysis data for the correlation of the carbon–tin coupling constants with Hammett σ constants are listed separately in Table 5 for the *para*- and *meta*-substituted derivatives. The one-bond tin coupling to C(1) is most sensitive to change in substituent, and gives an excellent correlation despite the remote position of this bond to the substituent group. The methyltin coupling is next most sensitive, also with low scatter in the correlation. It should be recalled that pairs of sites in aromatic compounds are doubly vicinal in that there are two paths for spin information to be transmitted through the σ bonds.

The sensitivities of the five measured coupling constants of the *para*-derivatives are in the order of their relative magnitudes with the correlation of the four-bond tin-C(4) coupling of smallest slope, but with a reasonably satisfactory correlation coefficient. The sensitivities of the three-bond (to C(3,5)) and two-bond (to C(2,6)) couplings are similar, but fall off as their magnitudes with the greatest scatter in the two-bond coupling data. The inversion in magnitudes between the two-bond coupling to C(2,6) and the three-bond coupling to C(3,5) is also seen with ^{199}Hg in diphenylmercury[35], ^{31}P in triphenylmethylphosphonium bromide[35], with ^{19}F in condensed fluoroaromatics[36–37], as well as with ^{1}H (ref. 38) and ^{13}C (ref. 39) in benzene and its derivatives.

Seven tin–carbon coupling constants are measured for each of the *meta*-derivatives. Again, the tin–carbon C(1) coupling constants are largest in magnitude and most sensitive to change in substituent, giving a good correlation with Hammett σ constants. The carbon-13 chemical shifts of C(1) in the *meta*-derivatives are also quite sensitive to change of substituent, and give a good correlation as well with Hammett

TABLE 5

TIN–CARBON COUPLING CONSTANT REGRESSION ANALYSIS PARAMETERS[a]

	r[b]	$\rho(Hz/\sigma)$[c]	$C(Hz)$[c]	n[d]
Para-derivatives vs. σ				
C(1)	0.995	−80.94	461.6	8
C(2,6)	0.508	− 4.02	39.1	8
C(3,5)	0.813	− 5.49	48.1	8
C(4)	0.910	2.77	11.6	8
Methyl	0.907	10.85	342.1	8
Meta-derivatives vs. σ				
C(1)	0.984	−90.62	465.5	5
C(2)	0.615	25.54	37.5	5
C(3)	0.889	33.55	49.2	5
C(4)	0.886	− 3.94	10.7	5
C(5)	0.184	− 2.68	49.4	5
C(6)	0.951	− 7.14	35.3	5
Methyl	0.960	17.28	339.3	5
All derivatives vs. σ				
C(1)	0.991	−80.62	462.4	12
Methyl	0.866	10.40	341.6	12

[a] Averaged values of the ^{117}Sn and ^{119}Sn coupling components were used where resolved. [b] Correlation coefficient. [c] Parameters of the equation $J = \rho\sigma + C$. [d] Number of compounds.

σ values (*vide supra*). There is also a strong interaction at the tin–methyl bond with a good correlation, despite the lack of change in the methyltin carbon-13 chemical shift with substituent. The C(1) carbon site is in a *meta*-relation to the substituent. The C(5) site, *meta* to both the substituent and the tin atom has a three-bond coupling to tin least sensitive to change of substituent, with no correlation with Hammett σ values. The second three-bond tin coupling, to the carbon holding the substituent, C(3), is next most sensitive to substituent changes after C(1). The two-bond coupling to C(2), a site *ortho* to both the substituent and to tin, is reasonably sensitive to substituent change, but the correlation coefficient is poor.

Our observations should be compared with those of the *para*-substituted fluorobenzenes for which only the one-bond carbon–fluorine coupling correlates with substituent parameters (Taft resonance parameters were used) and for the *meta*-derivatives in which even this correlation breaks down[5]. Combining our data for both *para*- and *meta*-derivatives, the correlation of Hammett σ constant with the tin–C(1) couplings is excellent (see Fig. 2).

The sensitivity of the raw coupling constant values to change in substituent gives an order which in the *para*-derivatives follows exactly the relative magnitudes of the couplings themselves to each carbon position. An alternative approach to the question of the sensitivity of the coupling constants to substituent change is considered in Table 6 where regression analysis parameters for differential couplings based upon $(J - J(\mathrm{H}))/J$ where J is the averaged tin-117, tin-119 coupling to the particular carbon listed and $J(\mathrm{H})$ the corresponding averaged coupling in the unsubstituted phenyltrimethyltin, are presented. This treatment in the case of the *para*-derivatives changes

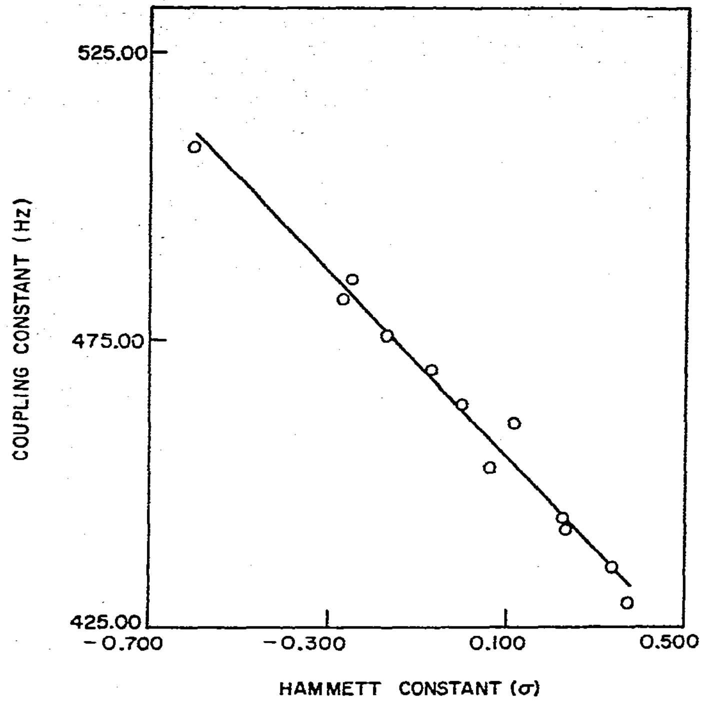


Fig. 2. Plot of $|J(\mathrm{Sn{-}^{13}C(1)})|$ coupling constants (averaged tin-117,119 values) *vs.* Hammett- σ constants for all derivatives except for *para*-trimethyltin.

the order of sensitivity of tin couplings from $C(1) > CH_3 > C(3,5) > C(2,6) > C(4)$ to $C(4) > C(1) > C(3,5) > C(2,6) > CH_3$ with the same couplings, $J(\mathrm{Sn{-}C(1)})$, $J(\mathrm{Sn{-}CH_3})$ and $J(\mathrm{Sn{-}C_4})$ yielding satisfactory correlations with the Hammett σ constants. In the *meta*-series the coupling to the substituent-holding carbon, C(3), also is seen in this treatment as the most sensitive, with the couplings to the two positions *ortho* to the substituent, C(2) and C(4), next.

The two fluoro derivatives studied in this investigation merit additional comment. In *para*-fluorophenyltrimethyltin, carbon–fluorine couplings as shown in Table 7 decrease in magnitude monotonically with increasing distance from the fluorine substituent, a trend generally observed in *para*-substituted fluorobenzenes[5]. In the *meta*-derivative, however, the decrease is not monotonic, with the fluorine coupling to C(6) greater than to C(1). Since normal resonance hybrid structures involving C(1) and C(3) with fluorine are prohibited, while a hybrid involving C(6) and C(3) with fluorine is not, the slightly larger value of the C(6) coupling can be rationalized. However, the fluorine coupling to C(5) is greater than to C(6). Sign information is necessary before a complete interpretation of these results can be achieved.

Carbon–proton couplings in benzenes have been correlated with proton couplings in ethylene using a relationship derived by Karabatsos for sp^2 hybridized carbon, $J(\mathrm{CH}) = 0.4\ J(\mathrm{HH})$[40], and the correlation has been applied to carbon–fluorine couplings in fluorobenzene and proton–fluorine couplings in vinyl fluoride[5]

TABLE 6

DIFFERENTIAL TIN–CARBON COUPLING CONSTANT REGRESSION ANALYSIS PARAMETERS[a]

	r^b	$\rho(Hz/\sigma)^c$	$C(Hz)^c$	n^d
Para-derivatives vs. σ				
C(1)	0.992	−0.168	−0.0065	8
C(2,6)	0.491	−0.092	0.0816	8
C(3,5)	0.809	−0.108	0.0351	8
C(4)	0.921	0.236	0.0626	8
Methyl	0.909	0.032	0.0064	8
Meta-derivatives vs. σ				
C(1)	0.922	−0.173	−0.0070	5
C(2)	0.649	0.476	0.0386	5
C(3)	0.887	0.552	0.0490	5
C(4)	0.860	0.426	−0.0095	5
C(5)	0.197	0.053	0.0588	5
C(6)	0.946	−0.218	−0.0075	5
Methyl	0.961	0.050	−0.0017	5
All derivatives vs. σ				
C(1)	0.981	−0.170	−0.0076	12
Methyl	0.868	0.030	0.0047	12

[a] Based on $\frac{J-J(\text{H})}{J}$, where J is the averaged tin-117, tin-119 coupling to the particular carbon listed, and J(H) is the corresponding averaged coupling in phenyltrimethyltin. [b] Correlation coefficient. [c] Parameters of the equation $J=\rho\sigma+C$. [d] Number of compounds.

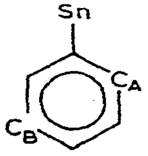
TABLE 7

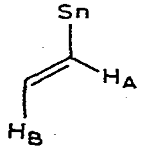
SOME $|(^{13}C-^{19}F)|$ COUPLING CONSTANTS (±0.25 Hz)[a]

Compounds	*C*(1)	*C*(2)	*C*(3)	*C*(4)	*C*(5)	*C*(6)	CH_3^b
p-F	4.2	6.7	19.2	246.8	19.2	6.7	—
m-F	2.7	17.4	250.4	21.1	6.5	3.2	—

[a] Neat liquids. [b] Coupling not resolved.

and has been used to predict carbon–metal couplings in organometallic compounds[32,35]. This relationship, if applied to the aromatic carbon–tin couplings in phenyltrimethyltin and proton–tin couplings in tetravinyltin [$J(\text{Sn–H}_A)=96.0$; $J(\text{Sn–H}_B)=183.1$ Hz[41]] predicts a geminal carbon–tin coupling of 38.4 and a vicinal coupling of 73.3 Hz, in the correct relative magnitudes, but in only qualitative agree-





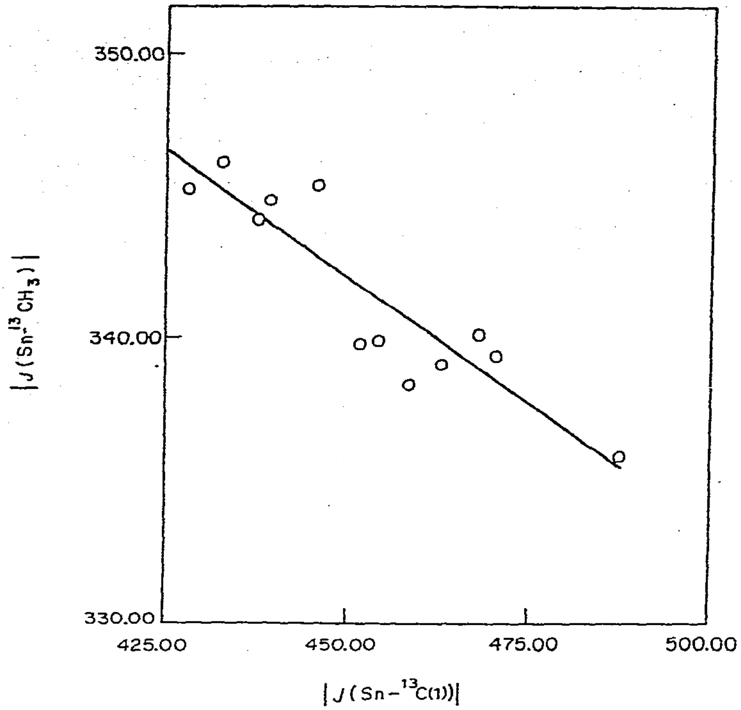
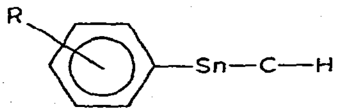


Fig. 3. Correlation of $|J(^{119}Sn\text{–}CH_3)|$ with $|J(^{119}Sn\text{–}C(1))|$. Regression analysis parameters: correlation coefficient, $r=0.909$; slope, $\rho=-0.134$; intercept, $C=403.6$ Hz; number of compounds = 12.

ment with the observed values (35.8 and 46.4 Hz, respectively). Some of the discrepancy likely arises from the greater importance of other mechanisms such as spin-orbit and dipole coupling for the tin–carbon spins than for the proton–carbon interaction.

Availability of both tin coupling data for C(1) and the methyl carbons permits an interesting determination of the effect of substituent change as registered at the tin atom. According to the isovalent hybridization concept of Bent[42], increasing electron demand in the system will bring about a redistribution of electron density at the tin atom in which 5*s*-character will tend to concentrate in the hybrid orbitals directed



toward the methyl group carbon atoms. Given a fixed amount of 5*s*-character to distribute, this should reduce the 5*s*-character in the hybrid orbital tin directs toward the C(1) carbon atom of the phenyl group*. In a Fermi contact-dominated mechanism for the spin–spin interaction, these electron density redistributions will be reflected in an increase in coupling constant with Hammett σ value for the trimethyltin carbons,

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* The total isotropic $|\psi ns(0)|^2$ at the tin nucleus as measured by the ^{119m}Sn Mössbauer Isomer Shift values remains constant within experimental error for our series[43], despite the anisotropic redistribution of 5*s*-electron density along the bonding axes as revealed by the coupling constant data.

and a corresponding decrease in coupling constant for the phenyltin C(1) carbon. Our observations are depicted in Fig. 3 in which the tin one-bond coupling constants (averaged tin-117,tin-119 values) are plotted against one another to give a straight line of negative slope. Although there is a roughly linear correlation between $|J(\text{Sn}{-}^{13}\text{C}(1))|$ and $|J(\text{Sn}{-}^{13}\text{CH}_3)|$, the line does not pass through the origin, indicating that at least one of the coupling constants may involve significant contributions from terms other than the Fermi contact interaction. Similar conclusions have been reached from studies of $|^1J(\text{Sn}{-}^{13}\text{C})|$ and $|^2J(\text{Sn}{-}\text{C}{-}^1\text{H})|$ in methyltin halides[24] and of $|^2J(\text{Sn}{-}\text{C}{-}^1\text{H})|$ and $|^3J(\text{Sn}{-}\text{C}{-}\text{C}{-}^1\text{H})|$ in ethyltin compounds[44]. Direct comparison of the one-bond tin–carbon coupling values in the thirteen compounds studied shows that the relative increase in value in going from the sp^3 to the sp^2 carbon corresponds closely to the 0.25/0.33 ratio of coefficients in the simple valence bond LCAO approach.

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