

Journal of Organometallic Chemistry, 99 (1975) 407–420
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PULSED FOURIER TRANSFORM NMR OF SUBSTITUTED ARYLTRIMETHYLTIN DERIVATIVES

IV*. PROTON AND CARBON-13 NMR DATA FOR *ortho*-, 2,6-, AND POLY-SUBSTITUTED ARYLTRIMETHYLTINS

C.D. SCHAEFFER, Jr.** and J.J. ZUCKERMAN*

Department of Chemistry, State University of New York at Albany, Albany, New York 12222 (U.S.A.)

(Received April 15th, 1975)

Summary

Proton and carbon-13 NMR data recorded in the Fourier transform mode are reported for ten *ortho*-substituted, six 2,6-disubstituted, and six miscellaneous polysubstituted aryltrimethyltin compounds. Although $|^1J(^{13}\text{C}-^1\text{H})|$ and $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$ coupling constants are rather insensitive to substituent variation, tin methyl proton chemical shifts reflect the increasing inductive effects as methyl-, chloro-, fluoro-, and trifluoromethyl-groups are brought into juxtaposition with the trimethyltin moiety. Resonances in the natural-abundance carbon-13 NMR spectra for the tin derivatives are assigned on the basis of additivity relationships, proton undecoupled spectra, and relative magnitudes of $|J(^{119}\text{Sn}-^{13}\text{C})|$ and $|J(^{13}\text{C}-^{19}\text{F})|$ coupling constants. Mutually deshielding γ -, δ -, and ϵ -effects in the carbon-13 chemical shifts of substituent carbons are rationalized in terms of steric crowding between the trimethyltin group and neighboring substituents. Deshieldings in ring carbons formally *para*- to conjugating substituents are discussed in terms of the steric inhibition of resonance model. Previous conclusions concerning lack of significant higher coordination at tin in aryltin derivatives bearing substituents with lone pair electrons are corroborated in this work.

Introduction

The understanding of steric hindrance and other non-bonded interactions in organometallic compounds and their reactions can be improved through the study of *ortho*- and polysubstituted phenyl derivatives where comparisons with

* For part III, see ref. 1.

** Present address: Department of Chemistry, Yale University, New Haven, CT 06520 (U.S.A.).

the corresponding *meta*- and *para*-substituted compounds are available.

Studies of aryltrimethyltins have been confined thus far to *meta*- and *para*-derivatives where chemical reactivity and spectroscopic data have been correlated with substituent constants in an attempt to generalize on the nature of the tin—phenyl bond. Recent studies of proton, carbon-13, and tin-119 NMR chemical shifts and coupling constants [1-4] have been interpreted in terms of transmission of substituent effects to the trimethyltin moiety.

Availability of *ortho*-, 2,6-, and polysubstituted aryltrimethyltins permits application of results from *meta*- and *para*-systems in an investigation of through space interactions in these crowded organometallic compounds. This paper reports tin methyl proton chemical shifts, $|^1J(^{13}\text{C}-^1\text{H})|$ and $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$ coupling constants, carbon-13 chemical shifts, and $|J(^{119}\text{Sn}-^{13}\text{C})|$ coupling constants for 22 derivatives. Tin-119 NMR chemical shifts and tin-119m Mössbauer spectroscopic results have been reported previously [4].

Experimental

Compounds

Preparation of the aryltrimethyltin derivatives has been described [4].

NMR parameters

All NMR parameters were measured in the fast Fourier transform (FFT) mode. Details in recording the proton [1] and carbon-13 [3] spectra of related compounds on the modified Varian HA-100D spectrometer equipped with Digilab pulse and data system (FTS/NMR-3) used in these studies have appeared elsewhere.

Tin methyl proton chemical shifts were obtained at 100 MHz with a resolution of ± 0.1 Hz. The results from at least three concentrations below 1% vol./vol. (liquids) or wt./vol. (solids) in CCl_4 were extrapolated to infinite dilution. Values of $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$ and $|^1J(^{13}\text{C}-^1\text{H})|$ were measured to ± 0.1 Hz. Solutions were 30% in CCl_4 .

Carbon-13 chemical shifts were recorded at 25.14 MHz with respect to 5% internal TMS and 10% internal benzene in separate determinations, and are believed accurate to ± 0.03 ppm. Values of $|J(^{119}\text{Sn}-^{13}\text{C})|$ and $|J(^{13}\text{C}-^{19}\text{F})|$ were obtained by sampling aromatic and trimethyltin carbon portions separately, employing minimal spectral bandwidths (1000 or 2000 Hz) and maximum transform lengths (16K or 32K) to insure high resolution. Coupling constants are believed accurate to ± 0.25 Hz. All carbon-13 parameters were obtained on neat liquids or saturated solutions of solids in CCl_4 . Ambient probe temperature was 39° .

Results

Table 1 lists tin methyl proton chemical shifts and $|^1J(^{13}\text{C}-^1\text{H})|$ and $|^2J(^{119}\text{Sn}-\text{C}-^1\text{H})|$ coupling constants obtained from the 100 MHz proton NMR spectra of the 22 compounds studied. Only a few measurements at 60 MHz have been previously reported for these derivatives [5-8], and no $|^1J(^{13}\text{C}-^1\text{H})|$ couplings have appeared before. Long-range $|J(^{119}\text{Sn}-^1\text{H})|$ and $|J(^{19}\text{F}-^1\text{H})|$ couplings have been detected in several cases. The coupling constant data are

TABLE 1

TIN METHYL PROTON CHEMICAL SHIFTS AND COUPLING CONSTANTS (± 0.1 Hz)

X	δ^a	$ ^1J(^{13}\text{C}-^1\text{H}) ^b$	$ ^2J(^{119}\text{Sn}-\text{C}-^1\text{H}) ^b$
H ^c	27.3	128.6	54.6
<i>o</i> -Cl	35.8	129.0	55.9
<i>o</i> -F ^d	33.4	129.2	56.6
<i>o</i> -CF ₃ ^e	33.3	129.2	54.1 ^f
<i>o</i> -CH ₃ ^g	29.9 ^h	128.3	53.8 ⁱ
<i>o</i> -C ₂ H ₅	29.5	128.4	53.5
<i>o</i> -OCH ₃ ^j	23.5	128.3	55.7 ^k
<i>o</i> -OC ₂ H ₅	23.9	128.3	55.7
<i>o</i> -N(CH ₃) ₂ ^l	22.3	127.8	54.6
<i>o</i> -Sn(CH ₃) ₃	30.5 ^m	128.5	53.0 ⁿ
2,6-Cl ₂	47.3	129.8	54.6
2,6-F ₂ ^o	32.3	129.1	57.4
2,6-(CF ₃) ₂ ^p	40.1	132.2	55.7
2,6-(CH ₃) ₂ ^q	34.5 ^r	128.8	53.0 ^s
2,6-(OCH ₃) ₂ ^t	22.7	128.4	57.0
2,6-(OC ₂ H ₅) ₂	26.6	128.2	56.9
2,3-(CH ₃) ₂ ^u	28.9	128.2	53.5
2,4-(CH ₃) ₂ ^v	27.3 ^w	128.2	53.5 ^x
3,4-(CH ₃) ₂ ^y	24.5	128.4	54.4
2,4,6-(CH ₃) ₃ ^z	32.3 ^{aa}	127.8	53.0 ^{bb}
2,4,6-(OCH ₃) ₃ ^{cc}	21.7	128.0	56.2
3,5-(CF ₃) ₂	40.9	129.6	56.2

^a Extrapolated to infinite dilution in CCl₄, relative to internal TMS in Hz. ^b 30% (vol./vol. or wt./vol.) in CCl₄. ^c Data were taken from ref. 1. ^d $|^5J(^{19}\text{F}-^1\text{H})| = 0.4$ Hz. ^e $|^6J(^{19}\text{F}-^1\text{H})| = 0.8$ Hz. ^f Lit. [5] 55.6 Hz. ^g δ CH₃ 237.8 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of CH₃ 125.3 Hz; $|^4J(^{119}\text{Sn}-^1\text{H})|$ of CH₃ 5.6 Hz. ^h Lit. [6] 18.2 Hz at 60 MHz. ⁱ Lit. [5] 53.9 Hz; 54.1 Hz [6]. ^j δ OCH₃ 377.7 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of OCH₃ 141.9 Hz. ^k Lit. [5] 56.4 Hz. ^l δ N(CH₃)₂ 261.5 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of N(CH₃)₂ 133.6 Hz. ^m Lit. [7] 0.31 ppm at 60 MHz. ⁿ Lit. [7] 53.0 Hz. ^o $|^5J(^{19}\text{F}-^1\text{H})| = 0.7$ Hz. ^p $|^6J(^{19}\text{F}-^1\text{H})| = 1.1$ Hz. ^q δ CH₃ 236.2 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of CH₃ 124.8 Hz; $|^4J(^{119}\text{Sn}-^1\text{H})|$ of CH₃ 6.0 Hz. ^r Lit. [6] 20.0 Hz at 60 MHz. ^s Lit. [6] 52.4 Hz. ^t δ OCH₃ 373.3 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of OCH₃ 143.0 Hz. ^u δ *o*-CH₃ 219.6 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of *o*-CH₃ 124.8 Hz; $|^4J(^{119}\text{Sn}-^1\text{H})|$ of *o*-CH₃ 7.4 Hz; δ *m*-CH₃ 227.2 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of *m*-CH₃ 126.0 Hz; $|^5J(^{119}\text{Sn}-^1\text{H})|$ of *m*-CH₃ 6.4 Hz. ^v δ *o*-CH₃ 232.4 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of *o*-CH₃ 124.8 Hz; $|^4J(^{119}\text{Sn}-^1\text{H})|$ of *o*-CH₃ 5.2 Hz; δ *p*-CH₃ 225.1 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of *p*-CH₃ 125.8 Hz. ^w Lit. [6] 16.0 Hz at 60 MHz. ^x Lit. [6] 53.4 Hz. ^y δ *m,p*-CH₃ 219.5 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of *m,p*-CH₃ 125.2 Hz. ^z δ *o*-CH₃ 230.3 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of *o*-CH₃ 125.2 Hz; $|^4J(^{119}\text{Sn}-^1\text{H})|$ of *o*-CH₃ 6.0 Hz; δ *p*-CH₃ 217.8 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of *p*-CH₃ 124.4 Hz. ^{aa} Lit. [8] 18.5 Hz at 60 MHz. ^{bb} Lit. [8] 52.5 Hz. ^{cc} δ *o*-OCH₃ 365.9 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of *o*-OCH₃ 143.2 Hz; δ *p*-OCH₃ 369.1 Hz; $|^1J(^{13}\text{C}-^1\text{H})|$ of *p*-OCH₃ 144.4 Hz.

rather insensitive to substituent variation, as in the corresponding *meta*- and *para*-derivatives [1]. In compounds bearing common methyl-, chloro-, fluoro-, and trifluoromethyl-substituents, the methyltin proton chemical shifts generally increase in the order $\delta(\textit{para}) < \delta(\textit{meta}) < \delta(\textit{ortho}) < \delta(2,6-)$, reflecting the increasing inductive effect which these substituents exert as they are brought into juxtaposition with the trimethyltin group.

Rationalization of the order for methoxy-, ethoxy-, and dimethylamino-substituents is not justified owing to insufficient numbers of common derivatives available. The methyltin proton chemical shifts are also rather sensitive to the number and position of methyl groups on the aromatic ring.

Carbon-13 chemical shifts at 25.14 MHz are listed in ppm relative to 5% internal tetramethylsilane (TMS) in Table 2. In this work, the trimethyltin group

TABLE 2
CARBON-13 CHEMICAL SHIFTS (± 0.03 ppm)^{a,b}

X	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH ₃
H ^c	141.53	135.66	128.07	128.07	128.07	135.66	-9.77
<i>o</i> -Cl	142.18	142.51	128.13	129.82	125.87	136.73	-8.46
<i>o</i> -F	126.78	167.54	114.20	130.47	124.20	136.64	-9.35
<i>o</i> -CF ₃ ^d	140.68	136.82	126.05	128.58	130.96	137.24	-7.96
<i>o</i> -CH ₃ ^e	140.88	143.69	128.86	128.54	125.08	135.66	-8.82
<i>o</i> -C ₂ H ₅ ^f	140.36	150.19	127.36	128.73	125.31	135.88	-8.40
<i>o</i> -OCH ₃ ^g	129.68	163.76	109.11	129.93	121.22	136.21	-9.26
<i>o</i> -OC ₂ H ₅ ^h	129.77	163.01	109.63	129.90	121.06	136.23	-9.12
<i>o</i> -N(CH ₃) ₂ ⁱ	141.63	160.30	120.21	129.55	125.29	136.40	-8.48
<i>o</i> -Sn(CH ₃) ₃ ^j	150.71	150.71	136.52	127.39	127.39	136.52	-7.20
2,6-Cl ₂	142.25	130.21	126.85	142.76	126.85	130.21	-4.17
2,6-F ₂	114.06	167.88	110.58	131.54	110.58	167.88	-8.03
2,6-(CF ₃) ₂ ^k	141.97	139.02	129.39	128.78	129.39	139.02	-3.84
2,6-(CH ₃) ₂ ^l	140.80	144.14	126.76	128.42	126.76	144.14	-5.21
2,6-(OCH ₃) ₂ ^{m,n}	116.28	165.18	103.43	131.11	103.43	165.18	-7.15
2,6-(OC ₂ H ₅) ₂ ^{m,o}	116.10	164.29	103.49	130.74	103.49	164.29	-6.75
2,3-(CH ₃) ₂ ^p	141.45	141.98	135.52	130.36	125.64	133.60	-8.48
2,4-(CH ₃) ₂ ^q	137.03	143.64	129.92	137.63	126.03	135.70	-8.84
3,4-(CH ₃) ₂ ^r	137.97	133.40	135.98	135.59	129.48	136.88	-9.69
2,4,6-(CH ₃) ₃ ^{m,s}	137.06	144.20	127.88	137.52	127.88	144.20	-5.27
2,4,6-(OCH ₃) ₃ ^{m,t}	106.77	165.69	90.37	163.41	90.37	165.69	-7.20
3,5-(CF ₃) ₂ ^u	146.64	136.18	131.78	122.79	131.78	136.18	-9.90

^aRelative to internal TMS (5%). Positive values are to increased frequency. ^bNeat liquids. ^cData were taken from ref. 3. ^d δ CF₃ 125.75. ^e δ CH₃ 24.58. ^f δ CH₂ 32.04; δ CH₃ 16.79. ^g δ OCH₃ 54.75. ^h δ OCH₂ 62.82; δ CH₃ 14.84. ⁱ δ N(CH₃)₂ 46.75. ^j50% (vol./vol.) in CCl₄. ^k δ CF₃ 125.38. ^l δ CH₃ 25.55. ^mSaturated solution in CCl₄. ⁿ δ OCH₃ 54.94. ^o δ OCH₂ 62.92; δ CH₃ 14.87. ^p δ *o*-CH₃ 22.23; δ *m*-CH₃ 20.59. ^q δ *o*-CH₃ 24.54; δ *p*-CH₃ 21.21. ^r δ *m,p*-(CH₃)₂ 19.49. ^s δ *o*-CH₃ 25.46; δ *p*-CH₃ 20.92. ^t δ *o*-OCH₃ 54.85; δ *p*-OCH₃ 54.61. ^u δ CF₃ 124.75.

is at the C(1) carbon. Positive values denote decreased shielding relative to TMS. Data for certain carbon-bearing substituent groups are also given. The carbon chemical shifts for phenyltrimethyltin have appeared in the literature [3,9,10]. In the *ortho*-derivatives, the ring carbons C(2) are, as expected, most sensitive to change in substituent (the carbon-13 shift range, $\Delta\delta = 31.88$ ppm), while C(1) is next most affected ($\Delta\delta = 23.93$ ppm). In the 2,6-disubstituted cases, the sensitivities of C(2,6) and C(1) to substituent alteration are similar ($\Delta\delta = 28.86$ and 28.19 ppm, respectively). Substituent groups containing highly electronegative atoms (F, O and N) generally give rise to substantial shielding of C(3) in the *ortho*- and 2,6-disubstituted derivatives, while the C(2) atoms are highly deshielded. These shielding trends are consistent with those encountered in other aromatic systems [11,12].

Table 3 compares the measured carbon-13 chemical shifts relative to 10% internal benzene (found) with those obtained assuming additivity (calcd.). The values calculated from data available for phenyltrimethyltin [3] and appropriate monosubstituted benzenes [13-16*] are in qualitative agreement, and it appears

* Incorrect values of chemical shifts for C(1) and C(2,6) of trifluoromethylbenzene have appeared in refs. 12 and 13. The correct values (determined in this work) should be: C(1), +2.6; C(2,6), -3.3 ppm. Data for this compound do appear elsewhere, but one source [15] omits the shift of C(1), and a recent compilation of carbon-13 spectra [16] erroneously assigns $|^4J(^{13}\text{C}-^{19}\text{F})|$ as 1.3 Hz. The correct coupling constants should be: $|^4J(^{19}\text{F}-^{13}\text{C}(3,5))|$, not detected; $|^5J(^{19}\text{F}-^{13}\text{C}(4))|$, 1.3 Hz.

TABLE 3
ADDITIVITY OF CARBON-13 CHEMICAL SHIFTS^a

X		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
H ^b	Found	+13.4	+7.5	-0.1	-0.1	-0.1	+7.5
o-Cl	Found	+14.0	+14.4	0.0	+1.7	-2.3	+8.6
	Calcd.	+13.8	+13.7	+0.3	+1.2	-2.0	+8.8
o-F	Found	-1.4	+39.4	-14.0	+2.3	-4.0	+8.4
	Calcd.	+0.5	+42.3	-13.0	+1.3	-4.6	+8.9
o-CF ₃	Found	+12.1	+8.2	-2.5	0.0	+2.4	+8.7
	Calcd.	+10.1	+10.1	-3.4	+0.2	+3.1	+7.8
o-CH ₃	Found	+12.8	+15.6	+0.8	+0.4	-3.0	+7.6
	Calcd.	+14.1	+16.4	+0.6	-0.2	-3.0	+7.4
o-C ₂ H ₅	Found	+11.9	+21.7	-1.1	+0.2	-3.2	+7.4
	Calcd. ^c	+12.8	+23.0	-0.7	-0.2	-2.8	+6.9
o-OCH ₃	Found	+1.5	+35.6	-19.0	+1.8	-7.0	+8.1
	Calcd.	-1.0	+38.9	-14.5	+0.9	-7.8	+8.5
o-OC ₂ H ₅	Found	+1.6	+34.8	-18.5	+1.7	-7.1	+8.1
	Calcd. ^d	-0.3	+38.5	-13.8	+1.0	-8.0	+8.6
o-N(CH ₃) ₂	Found	+13.6	+32.3	-7.8	+1.5	-2.8	+8.3
	Calcd. ^e	-2.1	+30.1	-15.6	+0.8	-11.9	+8.4
o-Sn(CH ₃) ₃	Found	+22.2	+22.2	+8.0	-1.1	-1.1	+8.0
	Calcd.	+20.9	+20.9	+7.4	-0.2	-0.2	+7.4
2,6-Cl ₂	Found	+13.8	+1.7	-1.7	+14.3	-1.7	+1.7
	Calcd.	+14.2	+15.0	-1.6	+2.5	-1.6	+15.0
2,6-F ₂	Found	-14.4	+39.4	-17.9	+3.0	-17.9	+39.4
	Calcd.	-12.4	+43.7	-17.5	+2.7	-17.5	+43.7
2,6-(CF ₃) ₂	Found	+13.0	+10.1	+0.6	0.0	+0.6	+10.1
	Calcd.	+6.8	+10.4	-0.2	+0.5	-0.2	+10.4
2,6-(CH ₃) ₂	Found	+12.8	+16.1	-1.3	+0.4	-1.3	+16.1
	Calcd.	+14.8	+16.3	-2.3	-0.3	-2.3	+16.3
2,6-(OCH ₃) ₂	Found	-17.9	+36.9	-24.8	+2.9	-24.8	+36.9
	Calcd.	-15.4	+39.9	-22.2	+1.9	-22.2	+39.9
2,6-(OC ₂ H ₅) ₂	Found	-12.1	+36.2	-24.7	+2.6	-24.7	+36.2
	Calcd. ^d	-14.0	+39.6	-21.7	+2.1	-21.7	+39.6
2,3-(CH ₃) ₂	Found	+13.3	+13.9	+7.4	+2.2	-2.5	+5.5
	Calcd.	+14.0	+17.1	+9.5	+0.5	-3.1	+4.5
2,4-(CH ₃) ₂	Found	+8.5	+15.1	+1.4	+9.1	-2.5	+7.2
	Calcd.	+11.2	+16.3	+1.3	+8.7	-2.3	+7.3
3,4-(CH ₃) ₂	Found	+9.5	+4.9	+7.1	+7.5	+1.0	+8.4
	Calcd.	+10.4	+8.1	+9.5	+9.5	+0.5	+10.5
2,4,6-(CH ₃) ₃	Found	+8.9	+16.0	-0.3	+9.4	-0.3	+16.0
	Calcd.	+11.9	+16.2	-1.6	+8.6	-1.6	+16.2
2,4,6-(OCH ₃) ₃	Found	-21.7	+37.2	-38.1	+34.9	-38.1	+37.2
	Calcd.	-23.1	+40.9	-36.6	+33.3	-36.6	+40.9
3,5-(CF ₃) ₂	Found	+17.8	+7.2	+2.9	-6.0	+2.9	+7.2
	Calcd.	+14.0	+7.4	+2.8	-6.7	+2.8	+7.4

^aRelative to 10% (vol./vol.) internal benzene (± 0.03 ppm). Positive shifts are to increased frequency. Data for monosubstituted aromatics are from ref. 13. ^bData were taken from ref. 3. ^cShifts for ethylbenzene were taken from ref. 31. ^dShifts for phenetole were taken from ref. 3. ^eShifts for *N,N*-dimethylaniline were taken from ref. 14.

TABLE 4

 $|J(^{119}\text{Sn}-^{13}\text{C})|$ COUPLING CONSTANTS (± 0.25 Hz)^{a,b}

X	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH ₃
H ^c	474.4	36.6	47.4	10.8	47.4	36.6	347.5
<i>o</i> -Cl	442.6	10.0	23.6	8.4	39.4	29.0	362.8
<i>o</i> -F	404.7	3.0	18.5	7.6	39.9	19.4	365.3
<i>o</i> -CF ₃ ^d	407.9	21.0	28.5	9.0	39.6	26.6	366.3
<i>o</i> -CH ₃ ^e	488.5	32.1	40.3	10.4	49.5	37.8	344.5
<i>o</i> -C ₂ H ₅ ^f	488.7	32.5	39.9	9.2	48.8	37.5	343.9
<i>o</i> -OCH ₃	463.9	4.5	23.2	7.7	47.4	26.2	358.6
<i>o</i> -OC ₂ H ₅	469.0	8.5	23.6	8.2	48.1	26.9	358.4
<i>o</i> -N(CH ₃) ₂	505.0	12.7	31.4	8.9	48.9	32.9	356.0
<i>o</i> -Sn(CH ₃) ₃ ^g	528.6	72.4	(48.2)	12.1	47.9	(65.0)	337.5
2,6-Cl ₂	407.7	^h	19.8	8.3	19.8	^h	371.0
2,6-F ₂	445.6	6.7	14.5	3.8	14.5	6.7	376.7
2,6-(CF ₃) ₂ ⁱ	402.5	12.8	22.5	6.4	22.5	12.8	375.0
2,6-(CH ₃) ₂ ^j	511.1	33.3	42.3	9.5	42.3	33.3	336.8
2,6-(OCH ₃) ₂ ^k	449.2	^h	23.2	^h	23.3	^h	365.6
2,6-(OC ₂ H ₅) ₂ ^k	456.5	^h	24.0	^h	24.0	^h	366.0
2,3-(CH ₃) ₂ ^l	499.7	32.4	41.0	10.7	54.4	38.7	342.5
2,4-(CH ₃) ₂ ^m	480.0	22.2	41.5	10.0	50.2	38.6	343.5
3,4-(CH ₃) ₂	460.0	36.0	50.2	9.0	49.6	37.3	345.1
2,4,6-(CH ₃) ₃ ⁿ	521.5	34.2	43.0	9.8	43.0	34.2	336.8
2,4,6-(OCH ₃) ₃ ^k	473.9	^h	24.9	4.5	24.9	^h	365.8
3,5-(CF ₃) ₂ ^o	403.2	34.6	42.6	^h	42.6	34.6	365.1

^a Neat liquids. ^b Couplings less than ca. 35 Hz were not consistently resolved into 117, 119 components.^c Data were taken from ref. 3. ^d $|^3J(\text{Sn}-^{13}\text{C})|$ to CF₃ 10.8 Hz. ^e $|^3J(\text{Sn}-^{13}\text{C})|$ to CH₃ 29.6 Hz. ^f $|^3J(\text{Sn}-^{13}\text{C})|$ to -CH₂ 28.8 Hz; $|^4J(\text{Sn}-^{13}\text{C})|$ to CH₃ = not detected. ^g Values in parentheses may be interchanged. ^h Not detected (<2.5 Hz). ⁱ $|^3J(\text{Sn}-^{13}\text{C})|$ to CF₃ 10.8 Hz. ^j $|^3J(\text{Sn}-^{13}\text{C})|$ to CH₃ 32.0 Hz. ^k Saturated solution in CCl₄. ^l $|^3J(\text{Sn}-^{13}\text{C})|$ to *o*-CH₃ 33.2 Hz; $|^4J(\text{Sn}-^{13}\text{C})|$ to *m*-CH₃ 7.4 Hz. ^m $|^3J(\text{Sn}-^{13}\text{C})|$ to *o*-CH₃ 28.9 Hz. ⁿ $|^3J(\text{Sn}-^{13}\text{C})|$ to *p*-CH₃ not detected. ^o $|^3J(\text{Sn}-^{13}\text{C})|$ to *p*-CH₃ not detected. ^p $|^4J(\text{Sn}-^{13}\text{C})|$ to CF₃ 4.1 Hz.

that assignments based upon additivity may be made with confidence in most of these systems.

Table 4 lists $|J(^{119}\text{Sn}-^{13}\text{C})|$ coupling constants for ring and substituent carbons. Additional $|J(^{13}\text{C}-^{19}\text{F})|$ couplings confirmed ring carbon assignments when fluoro- or trifluoromethyl-substituents were present, and these data appear in Table 5. The magnitude of $|^1J(^{119}\text{Sn}-^{13}\text{C}(1))|$ is most sensitive to substituent variation for all derivatives studied, with $\Delta|^1J|$ ca. 120 Hz. As in our previous study [3], an increase in $|^1J(^{119}\text{Sn}-^{13}\text{C}(1))|$ accompanies a decrease in

TABLE 5

 $|J(^{13}\text{C}-^{19}\text{F})|$ COUPLING CONSTANTS (± 0.25 Hz)^a

X	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH ₃
<i>o</i> -F	43.8	234.7	27.4	7.5	2.8	14.6	1.7
2,6-F ₂	46.4	238.2, 18.4	27.7, 3.8	9.1	27.7, 3.8	238.2, 18.4	2.5
<i>o</i> -CF ₃ ^b	4.2	30.1	4.6	^c	1.0	^c	2.7
2,6-(CF ₃) ₂ ^d	3.2	12.8	6.1	^c	6.1	12.8	3.8
3,5-(CF ₃) ₂ ^e	^c	1.6	32.7	3.9	32.7	1.6	^c

^a Neat liquids. ^b $|^1J(^{13}\text{C}-^{19}\text{F})|$ of CF₃ 273.2 Hz. ^c Not detected (<2.5 Hz). ^d $|^1J(^{13}\text{C}-^{19}\text{F})|$ of CF₃ 274.0 Hz. ^e $|^1J(^{13}\text{C}-^{19}\text{F})|$ of CF₃ 272.5 Hz.

$|^1J(^{119}\text{Sn}-^{13}\text{CH}_3)|$, as has also been observed in series of tetraalkyltins [17]. A gradual monotonic decrease of $|^1J(^{119}\text{Sn}-^{13}\text{C}(1))|$ in the order $J(\textit{para-}) > J(\textit{meta-}) > J(\textit{ortho-})$ is observed for fluoro- and methoxy-, while $|^1J(^{119}\text{Sn}-^{13}\text{CH}_3)|$ for these compounds increases in the same order. Lack of complete series of common substituents precludes further meaningful comparisons.

The wide variation in $|^2J(^{119}\text{Sn}-\text{C}-^{13}\text{C}(2))|$ ($\Delta|^2J|$ ca. 70 Hz) is striking; 2- or 2,6-substitution with substituents containing highly electronegative atoms frequently reduces the magnitude of the two-bond coupling below the limit of detection (ca. 3 Hz), while substitution by 2-trimethyltin effectively doubles $|^2J(^{119}\text{Sn}-\text{C}-^{13}\text{C}(2))|$.

In the *meta*- and *para*-derivatives the relative magnitude of the tin coupling to the ring carbons is $|^2J| < |^3J|$ [3,9], similar to that reported for phenyltin trichloride, *para*-tolyltin trichloride [18], triphenyltin chloride and diphenyltin dichloride [19], and for substituted benzyltrimethyltins [9]. In this work the order in the *ortho*-derivatives is often reversed, with the $|^2J|$ to C(6) frequently larger than the $|^3J|$ to C(3)*. In the *ortho*-trimethyltin derivative, $|^2J(\text{C}(2))| > |^3J(\text{C}(5))|$. For corresponding pairs, however, the order remains $|^3J| > |^2J|$, except in the *ortho*-trimethyltin derivative.

Discussion

Assignment of aromatic carbon resonances

Assignments of the aromatic carbon resonances in the aryltrimethyltins reported here are based upon (1) substituent effects and additivity relationships among the chemical shifts, (2) observations from proton undecoupled spectra, and (3) relative magnitudes of $|J(^{119}\text{Sn}-^{13}\text{C})|$ and $|J(^{13}\text{C}-^{19}\text{F})|$ coupling constants. Contrary to earlier work [11] in which additivity in *ortho*- and polysubstituted aromatic systems failed to predict shielding effects, the two sets of data in Table 3 are in good qualitative agreement. The use of additivity data alone in assigning certain ring carbons is hazardous, however [cf., C(2,6) and C(4) in the 2,6-dichloro-derivative].

Trends in $|J(^{119}\text{Sn}-^{13}\text{C})|$ have proved useful in confirming assignments based upon additivity. The coupling order for ring carbons is similar to that of *meta*- and *para*-derivatives [3,9], although caution must be exercised when comparing two- and three-bond couplings over different bond pathways (vide supra).

The relative magnitudes of $|J(^{13}\text{C}-^{19}\text{F})|$ in fluoro- and trifluoromethyl-substituted aryltrimethyltins are also valuable in confirming assignments of carbon resonances. In this study, $|J(^{13}\text{C}-^{19}\text{F})|$ decreases in the order $|^1J| > |^2J| > |^3J| > |^4J|$ (see Table 5). In the trifluoromethyl-derivatives, however, $|^5J| > |^4J|$, as in *ortho*-substituted trifluoromethylbenzenes [20].

The proton-noise decoupled carbon-13 spectrum of *ortho*-fluorophenyltrimethyltin shown in Figs. 1-3 illustrates the principles of assignment discussed above. Additivity predicts the shielding values of the six non-equivalent ring carbons (Fig. 1) reasonably well. Carbon C(2) bearing the fluoro-substituent is readily assigned from the direct $|^1J(^{13}\text{C}-^{19}\text{F})|$ coupling. In addition, C(2) dis-

* Recent studies of tin-carbon couplings in furyl and thienyl derivatives have supported the order $|^1J| > |^2J| > |^3J|$, although some of the ring carbon assignments are tentative [10].

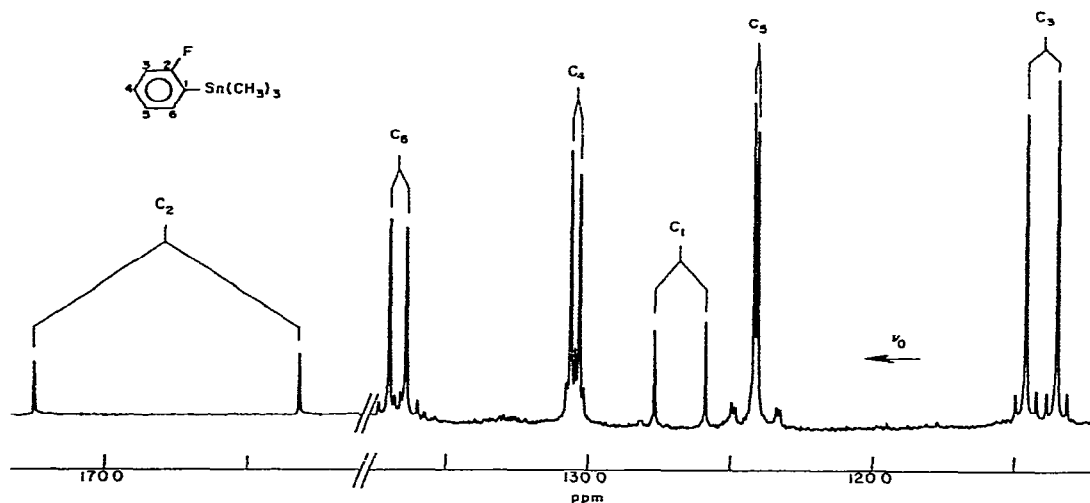


Fig. 1. Proton-decoupled natural abundance carbon-13 NMR spectrum of aromatic carbons of *ortho*-fluorophenyltrimethyltin. This 16K Fourier transform required 15 000 pulses over a spectral bandwidth of 2 000 Hz.

plays the typically large deshielding associated with carbons directly attached to highly electronegative substituents [11]. The magnitude of $|^1J(^{119}\text{Sn}-^{13}\text{C})|$ confirms the assignment of C(1) (see Fig. 2). The relatively low intensities of C(1) and C(2) (which appear unchanged in the proton undecoupled spectrum) are indicative of the absence of signal-enhancing nuclear Overhauser effect with carbons lacking a directly-bonded proton [21]. Carbon C(4) displays the smallest coupling to tin, with a magnitude characteristic of a four-bond interaction, while C(5) exhibits a four-bond coupling of expected magnitude with fluorine. The C(3) and C(6) resonances may be assigned using related arguments. Caution must be

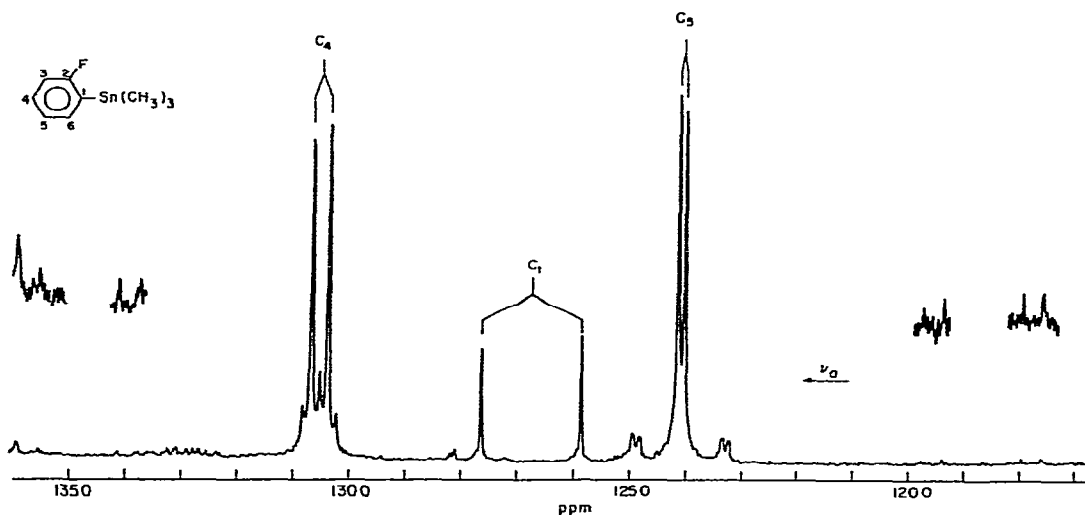


Fig. 2. Expansion of Fig. 1, showing $|^1J(^{117,119}\text{Sn}-^{13}\text{C})|$ couplings to C(1).

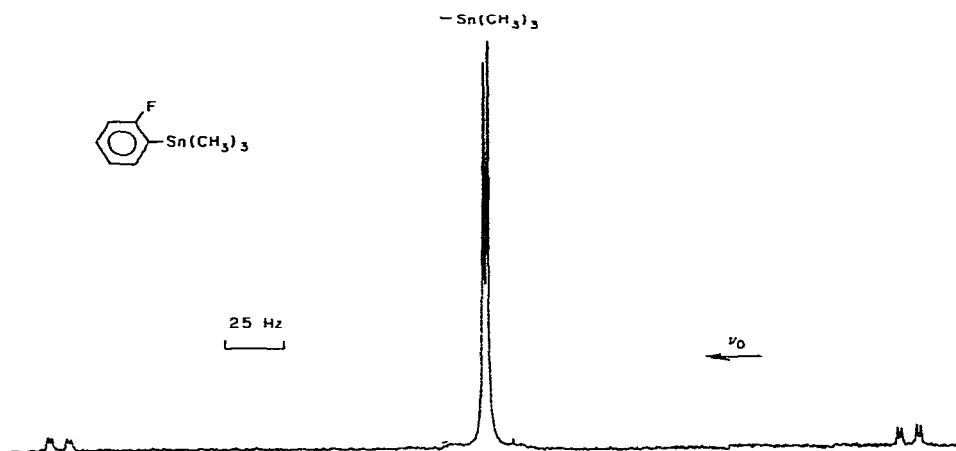


Fig. 3. Trimethyltin carbons of *ortho*-fluorophenyltrimethyltin, showing $|^4J(^{19}\text{F}-^{13}\text{C})|$ coupling.

exercised in these examples, since the two-bond, tin coupling to C(6) is clearly of greater magnitude than the three-bond coupling to C(3). Fig. 3 shows the small, four-bond fluorine coupling with the trimethyltin group carbon atoms. Analogous arguments may be employed in the assignment of the aromatic carbons in 2,6-bis(trifluoromethyl)phenyltrimethyltin (Fig. 4).

It is apparent that tin-carbon coupling constants will prove valuable in assigning structure and conformation in organotin compounds, when used in conjunction with chemical shift data*. Recent work on tin derivatives of indan [23], tetralin [23], and naphthalene [24], has shown promise in this direction.

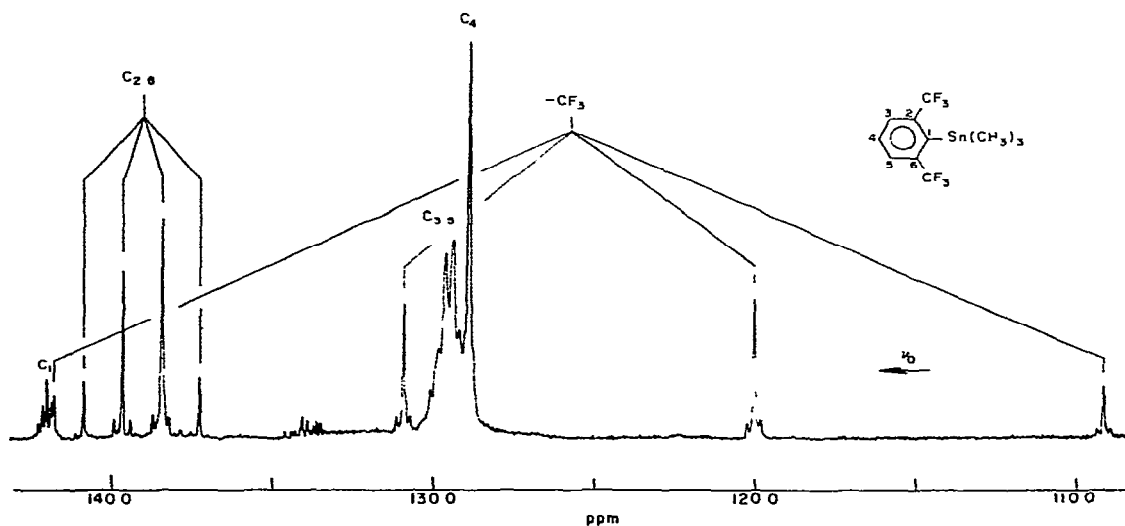


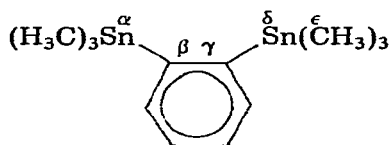
Fig. 4. Proton-decoupled natural abundance carbon-13 NMR spectrum of aromatic carbons of 2,6-bis(trifluoromethyl)phenyltrimethyltin. Data are similar to Fig. 1.

* The large magnitude of $|^1J(^{119}\text{Sn}-^{13}\text{C})|$ is indicative of a direct tin-carbon bond, and $|^3J(^{119}\text{Sn}-\text{C}-\text{C}-^{13}\text{C})|$ displays a dependence on dihedral angle [22].

Steric bulk of the trimethyltin group

Nonbonded interactions in Group IVB derivatives have long been of interest [25]. Line broadening in the fluorine-19 NMR spectrum of bis(pentafluorophenyl)diphenyltin and in related compounds has been rationalized in terms of steric hindrance to rotation about tin-aryl carbon bonds [26]. Epoxidation and hydroboration reactions of *syn*-7-substituted norbornenes have been used as probes of the steric bulk of a variety of substituents, including the trimethyltin group. Steric hindrance to these reactions was found to decrease in the order: $-t\text{-C}_4\text{H}_9 > -\text{CH}_3 > -\text{Br} > -\text{Sn}(\text{CH}_3)_3 > -\text{Cl} > -\text{H}$, suggesting that the large covalent radius of tin is more than offset by the length of the tin-carbon bond [27]. This rationalization of the relatively small effective steric bulk of the $-\text{Sn}(\text{CH}_3)_3$ group has been invoked in recent studies of rotamer populations and $|^3J(^{119}\text{Sn}-^{13}\text{C})|$ coupling constants in tetraalkyltins [17]. On the other hand, the ultraviolet spectrum of 1,2-bis(trimethyltin)benzene contains features apparently characteristic of a distorted phenyl ring, and interactions of the methyl groups were judged to be at least as severe as in 1,2-bis(*t*-butyl)benzene [7].

Our NMR data support methyl group interaction in 1,2-bis(trimethyltin)benzene. Substitution of $-\text{Sn}(\text{CH}_3)_3$ for $-\text{H}$ at the *ortho*-position in phenyltrimethyltin:



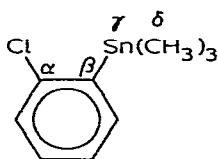
induces an ϵ -shift of + 2.6 ppm (deshielding) in the methyl carbons (see Table 2). Similar deshielding effects in methyl carbons at δ - and ϵ -positions have been interpreted in terms of steric crowding in methylnaphthalenes [28], alkyl-substituted anisoles [29], and in substituted methylphenyl sulfides, sulfoxides, and sulfones [30]. Tin-carbon couplings also reflect substantial steric interactions. An increase of 54.2 Hz in the one-bond coupling to C(1) on trimethyltin substitution at the *ortho*-position is accompanied by a doubling in magnitude of the coupling to C(2). These drastic alterations are most easily explained in terms of steric interactions of the adjacent trimethyltin groups causing distortions of the aromatic ring. The methyltin proton chemical shifts in Table 1 reflect these trends, although the differences are smaller.

Ortho-substitution of a methyl or ethyl group in phenyltrimethyltin has a negligible effect on the carbon shielding at C(6). Apparently, little γ -effect results from C(6)-trimethyltin interaction as a consequence of increased steric congestion at C(2). This is contrary to the observations reported for *ortho*-substituted anisoles, where such γ -steric effects shield the C(6) carbon by ca. 3 ppm [29]. The relatively long tin-aryl bond apparently reduces the steric interaction with C(6) in the *ortho*-substituted aryltrimethyltins. However, a γ -shielding effect of -3.5 ppm is detected in the tin-119 NMR chemical shift of 1,2-bis(trimethyltin)benzene relative to phenyltrimethyltin [4], consistent with steric interaction between the trimethyltin groups (*vide supra*).

The effect of adjacent alkyl group substitution on tin methyl carbon chemical shifts may be understood in terms of steric interactions. In the 2,6-dimethyl

system, the interacting substituent and tin methyl groups are δ - to each other, and a deshielding of the tin methyl carbons by +4.6 ppm occurs relative to phenyltrimethyltin. In the *ortho*-methyl derivative, the δ -deshielding is ca. +1.0 ppm. Likewise, the substituent methyl carbon resonance in 2,6-dimethylphenyltrimethyltin is ca. +1.0 ppm deshielded relative to the *ortho*-methyl derivative, and +4.2 ppm relative to the methyl carbon in toluene [31]. Similar effects occur for the 2,4,6-trimethyl derivative. This behavior indicates a mutual methyl—trimethyltin δ -interaction in these derivatives. Methyl substitution remote from the trimethyltin group (e.g., in the 2,3-, 2,4-, and 3,4-positions) has only negligible influence on the tin methyl shieldings. An analogous methyl—methoxy δ -interaction has been reported in *ortho*- and 2,6-dimethyl-substituted anisoles [29], and a $\text{CH}_3\text{—SCH}_3$ δ -interaction has been observed in 2,4,6-trimethylphenyl methylsulfide [30]. In the *ortho*-ethyl derivative the tin methyl carbons and the terminal methyl carbon of the substituent are mutually ϵ , and undergo deshieldings of +1.4 (relative to phenyltrimethyltin) and +1.0 ppm (relative to the terminal methyl carbon in ethylbenzene) [31], respectively. This ϵ -effect is ca. one-half that observed in 1,2-bis(trimethyltin)benzene (vide supra). Similar ϵ -effects have been reported for isopropyl-substituted anisoles [29] and methyl phenyl sulfides [30].

Effects in halogen-substituted derivatives are more difficult to rationalize. Introduction of —Cl in the 2-position of phenyltrimethyltin deshields the δ -tin

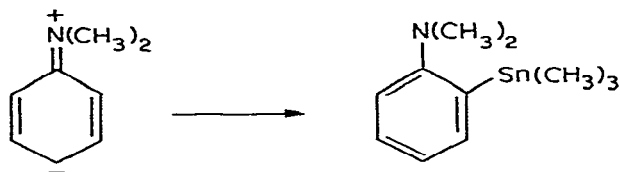


methyl carbons by +1.3 ppm, and by an additional +4.3 ppm in the 2,6-derivative. Likewise, the tin methyl carbons of the 2- and 2,6- CF_3 derivatives are deshielded by +1.8 and an additional +4.1 ppm, respectively. However, similar deshieldings are registered at the —CF_3 carbons (relative to the substituent carbon in trifluoromethyltoluene) [20] in both the 2- and 2,6-derivatives, i.e., the small δ -effect is not accentuated by introduction of a second —CF_3 group. Moreover, the tin atoms in the γ -position also undergo increasing deshielding on *ortho*- and 2,6-substitution by these groups, contrary to that expected from steric interactions, suggesting that the origin of the observed deshieldings lies in inductive effects. Assuming that the effective electronegativities of —Cl and —CF_3 are roughly equal, then the changes observed in the tin methyl carbon shifts may be attributed to electronic effects associated with disubstitution. A through-space $^{119}\text{Sn}\text{—}^{19}\text{F}$ coupling mechanism [32] made possible by steric interaction has recently been ruled out in *ortho*-trifluoromethylphenyltin systems [33].

Steric interactions determine methyl carbon chemical shifts in derivatives bearing *ortho*- and 2,6- methoxy-, ethoxy-, and dimethylamino-substituents, however. *Ortho*-substitution by $\text{—N(CH}_3)_2$ deshields the tin methyl carbons by +1.3 ppm, while a +6.4 ppm deshielding occurs in the substituent dimethylamino-carbons relative to *N,N*-dimethylaniline [20]. The methyl groups are formally ϵ - to each other. The tin-119 resonance shows the shielding effect

(-16.0 ppm) [4] associated with an atom in a γ -position subjected to steric crowding. Substitution of methoxy- and ethoxy-groups at the *ortho*- and 2,6-positions leads to stepwise deshielding of the tin methyl carbons ($-\text{OCH}_3$, $+0.5$ and $+2.6$ ppm vs. phenyltrimethyltin; $-\text{OC}_2\text{H}_5$, $+0.7$ and $+3.0$ ppm), but the shieldings of the substituent methyl carbons remain invariant throughout. Although the tin-119 resonances exhibit the expected γ -shielding effects which approximately triple in magnitude on 2,6-disubstitution [4], an interpretation based solely upon steric effects is not justified.

Examination of Table 3 reveals that the ring carbon shieldings of several of the *ortho*-substituted derivatives are not predicted accurately by additivity relationships. In particular, the *ortho*-methoxy-, ethoxy-, and dimethylamino-derivatives deviate. This behavior has also been observed in substituted *N,N*-dimethylanilines [34], nitrobenzenes [35], and anisoles [36], where it has been attributed to the steric inhibition of resonance by neighboring bulky substituents which prevent the coplanarity of the conjugated system. In the *ortho*-trimethyltin-substituted anisole, phenetole, and dimethylaniline derivatives in this study, the deshielding observed at the C(5) site *para*- to the conjugating substituent relative to the corresponding position in the parent compound [C(4)]

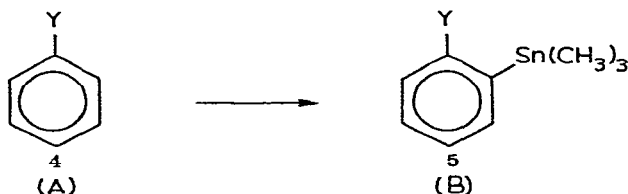


is consistent with a decrease in the contribution from the planar hybrid structure expected in the unhindered case. Trimethyltin substitution at C(2) in toluene, on the other hand, has virtually no effect on the *para*-carbon shielding at C(5) (see Table 6). Trimethyltin substitution in chlorobenzene and trifluoromethylbenzene induces shielding effects at C(5) consistent with the small electron-releasing effect of the trimethyltin group. However, a deshielding of $+8.6$ ppm occurs in the dimethylamino case, while smaller effects occur with anisole and phenetole as well. Decreases in $|^1J(^{13}\text{C}-^1\text{H})|$ are also consistent with the steric inhibition of resonance model [37].

The relative contributions of steric and electronic effects to the magnitude of $|J(^{119}\text{Sn}-^{13}\text{C})|$ in these systems are difficult to evaluate. *ortho*-Methyl group substitution in phenyltrimethyltin results in a 14.1 Hz increase in $|^1J(^{119}\text{Sn}-^{13}\text{C}(1))|$, while 2,6-disubstitution results in a 36.7 Hz increase, 6.5 Hz greater than that predicted by an additive effect of *ortho*-substitution. Assuming that the electronic effects are in fact additive, the remaining 6.5 Hz may be attributed to steric interactions of methyl and trimethyltin moieties as in *ortho*-bis-(trimethyltin)benzene (*vide supra*). Decreases of $|^1J(^{119}\text{Sn}-^{13}\text{CH}_3)|$ in the methyl derivatives are also consistent with a steric interaction. For tin derivatives bearing electronegative atoms, decreases are observed in one-bond tin couplings to C(1), but comparisons lead to mixed conclusions concerning steric hindrance. More information on the nature of the coupling mechanism is needed before meaningful generalizations may be drawn.

The chemical shifts for the aryltrimethyltins in Table 2 may be compared

TABLE 6
 CARBON-13 CHEMICAL SHIFT AND $|^1J(^{13}\text{C}-^1\text{H})|$ COUPLING CONSTANT COMPARISONS IN



	Y	$\delta \text{ C(p)}$ (ppm) ^a	$ ^1J(^{13}\text{C}-^1\text{H}) $ (Hz) ^b
(A)	CH ₃	125.34	125.8
(B)	CH ₃	125.08	125.3
(A)	Cl	126.65	
(B)	Cl	125.87	
(A)	CF ₃	131.72	
(B)	CF ₃	130.96	
(A)	OCH ₃	120.48	143.2
(B)	OCH ₃	121.22	141.9
(A)	OC ₂ H ₅	120.62	
(B)	OC ₂ H ₅	121.06	
(A)	N(CH ₃) ₂	116.70	134.5
(B)	N(CH ₃) ₂	125.29	133.6

^a $\delta \text{ C(p)}$ for (A) (parent monosubstituted aromatic compound) is $\delta \text{ C(4)}$ and for (B) (*ortho*-substituted aryltrimethyltin derivative) is $\delta \text{ C(5)}$. Carbon-13 chemical shifts for (A) were taken from refs. 11, 14, and 20. ^b Carbon-13 coupling constants to Y-methyl protons. Values for (A) were taken from ref. 37.

with those of the parent aromatic compounds [12,13]. The substituent shielding effects^{*} reveal the following trends: (1) Carbons C(1) (α -) are generally deshielded by 12-15 ppm, (2) C(2) and C(6) (β -) are deshielded by 4-9 ppm, (3) C(3) and C(5) (γ -) are shielded by 0.1-4.0 ppm, and (4) C(4) (δ -) are deshielded by 0.4-0.8 ppm. The α -, β -, and γ -effects are similar to those encountered in *meta*- and *para*-substituted aryltrimethyltins [3,38]. The constancy of the substituent shieldings in structurally similar compounds has facilitated the assignments of carbon-13 spectra of complex organotin [17,22,23].

Conclusion

The potential for direct, across-space interaction with tin exists for fluoro-, chloro-, trifluoromethyl-, methoxy-, ethoxy-, and dimethylamino-substituents which possess lone pair electrons. Previously recorded [4] changes in tin-119 NMR chemical shifts, $|J(^{119}\text{Sn}-^{19}\text{F})|$ coupling constants, and tin-119m Mössbauer Isomer Shifts and Quadrupole Splittings have been rationalized in terms

* The substituent shielding effect is defined as the change in shielding of a carbon atom n upon substitution in the parent hydrocarbon:

$$\Delta\delta_n = \delta_n (\text{aryltrimethyltin derivative}) - \delta_n (\text{parent aromatic compound})$$

Positive values are deshielded relative to the parent aromatic compound.

of electronegativity differences and steric effects, and no significant higher coordination at the tin atom was detected. Our proton and carbon-13 NMR results reported here confirm these conclusions.

Acknowledgements

We thank M&T Chemicals, Inc. for the donation of the organotin starting materials. Our work is supported by the National Science Foundation through Grant No. GP-16,544. Mr. K. Wursthorn of SUNY-Albany kindly supplied samples of *ortho*-bis(trimethyltin)benzene and 2,6-dichlorophenyltrimethyltin. Dr. E.A. Williams and J.D. Cargioli of the General Electric Research and Development Center at Schenectady assisted in obtaining several carbon-13 spectra.

References

- 1 C.D. Schaeffer, Jr. and J.J. Zuckerman, *J. Organometal. Chem.*, 78 (1974) 373.
- 2 C.D. Schaeffer, Jr. and J.J. Zuckerman, *J. Organometal. Chem.*, 47 (1973) C1.
- 3 C.D. Schaeffer, Jr. and J.J. Zuckerman, *J. Organometal. Chem.*, 55 (1973) 97; 59 (1973) C40.
- 4 H.-J. Kroth, H. Schumann, H.G. Kuivila, C.D. Schaeffer, Jr. and J.J. Zuckerman, *J. Amer. Chem. Soc.*, 97 (1975) 1754
- 5 T. Chivers and J.R. Sams, *Chem. Commun.*, (1969) 249; *J. Chem. Soc. A*, (1970) 928.
- 6 S. Boué, M. Gielen and J. Nasielski, *Bull. Soc. Chim. Belg.*, 76 (1967) 559.
- 7 A.B. Evin and D. Seyferth, *J. Amer. Chem. Soc.*, 89 (1967) 952.
- 8 M.R. Kula, E. Amberger and K.K. Mayer, *Chem. Ber.*, 98 (1965) 634.
- 9 D. Doddrell, M.L. Bullpitt, C.J. Moore, C.W. Fong, W. Kitching, W. Adcock and B.D. Gupta, *Tetrahedron Lett.*, (1973) 665
- 10 D. Doddrell, K.G. Lewis, C.E. Mulquoney, W. Adcock, W. Kitching and M. Bullpitt, *Aust. J. Chem.*, 27 (1974) 417.
- 11 J.B. Stothers, *Carbon-13 NMR Spectroscopy*, Academic Press, New York, N.Y., 1972.
- 12 G.C. Levy and G.L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley-Interscience, New York, N.Y., 1972.
- 13 G.L. Nelson, G.C. Levy and J.D. Cargioli, *J. Amer. Chem. Soc.*, 94 (1972) 3089.
- 14 G.E. Maciel and J.J. Natterstad, *J. Chem. Phys.*, 42 (1965) 2427.
- 15 G. Miyajima, Y. Sasaki and M. Suzuki, *Chem. Pharm. Bull.*, 19 (1971) 2301
- 16 L.F. Johnson and W.C. Jankowski, *Carbon-13 NMR Spectra*, Wiley-Interscience, New York, N.Y., 1972, spectrum number 225.
- 17 R.J. Mynott, J.L. Considine, H.G. Kuivila and R.H. Sarma, unpublished results.
- 18 G. Matsubayashi and T. Tanaka, *Spectrochim. Acta, Part A*, 30 (1974) 869.
- 19 T.N. Mitchell, *J. Organometal. Chem.*, 59 (1973) 189.
- 20 C.D. Schaeffer, Jr., C.H. Yoder and J.J. Zuckerman, unpublished results.
- 21 J.H. Noggle and R.E. Schirmer, "The Nuclear Overhauser Effect, Chemical Applications," Academic Press, New York, N.Y., 1971.
- 22 D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, C.-H. Lee, R.J. Mynott, J.L. Considine, H.G. Kuivila and R.H. Sarma, *J. Amer. Chem. Soc.*, 96 (1974) 1640.
- 23 W. Adcock, B.D. Gupta, W. Kitching, D. Doddrell and M. Geckle, *J. Amer. Chem. Soc.*, 96 (1974) 7360.
- 24 C.D. Schaeffer, Jr. and J.J. Zuckerman, unpublished results.
- 25 C.F. Shaw, III and A.L. Allred, *Organometal. Chem. Rev. A*, 5 (1970) 95.
- 26 D.E. Fenton, A.G. Massey, K.W. Jolley and L.H. Sutcliffe, *Chem. Commun.*, (1967) 1097.
- 27 D.D. Davis, A.J. Surmatis and G.L. Robertson, *J. Organometal. Chem.*, 46 (1972) C9.
- 28 S.H. Grover, J.P. Guthrie, J.B. Stothers and C.T. Tan, *J. Magn. Resonance*, 10 (1973) 227.
- 29 G.W. Buchanan, G. Montaudo and P. Finocchiaro, *Can. J. Chem.*, 52 (1974) 767.
- 30 G.W. Buchanan, C. Reyes-Zamora and D.E. Clarke, *Can. J. Chem.*, 52 (1974) 3895.
- 31 D. Lauer, E.L. Motell, D.D. Traficante and G.E. Maciel, *J. Amer. Chem. Soc.*, 94 (1972) 5335.
- 32 W. McFarlane, *Chem. Commun.*, (1971) 609.
- 33 M. Barnard, P.J. Smith and R.F.M. White, *J. Organometal. Chem.*, 77 (1974) 189.
- 34 P.C. Lauterbur, *J. Chem. Phys.*, 38 (1963) 1415.
- 35 P.C. Lauterbur, *J. Chem. Phys.*, 38 (1963) 1432.
- 36 K.S. Dhani and J.B. Stothers, *Can. J. Chem.*, 44 (1966) 2855.
- 37 C.H. Yoder and B.A. Kaduk, *Tetrahedron Lett.*, (1970) 3711.
- 38 D.E. Axelson, S.A. Kandil and C.E. Holloway, *Can. J. Chem.*, 52 (1974) 2968.