Journal of Organometallic Chemistry, 78 (1974) 373—383

PULSED FOURIER TRANSFORM NMR OF SUBSTITUTED ARYLTRIMETHYLTIN DERIVATIVES

III*. PROTON DATA AT 100 MHz AND THE DERIVED HAMMETT σ-CONSTANT OF THE TRIMETHYLTIN GROUP

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(Received January 22nd, 1974)

Summary

Proton NMR data at 100 MHz are reported for thirteen *para*- and *meta*-substituted phenyltrimethyltin compounds, $XC_6H_4Sn(CH_3)_3$, where X = *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*-$Sn(CH_3)_3$. Correlation coefficients with Hammett σ-constants of greater than 0.95 are obtained with the methyltin proton chemical shifts and coupling constants to carbon $[^1J(^{13}C—^1H)]$ and tin $[^2J(Sn—C—^1H)]$. Solvent effects and other extraneous factors invalidate comparisons of ρ values in terms of the relative attenuation of the transmission of substituent effects through homologous carbon, silicon, germanium and tin systems, but coupling constant data reflect a diminution of ca. one tenthfold per bond in the order $\rho[C(1)—Sn] > \rho\ [Sn—C] > \rho\ [C—H]$. Satisfactory correlations ($r > 0.95$) are obtained in this series of closely-related compounds among the conventionally recorded two-bond, $^2J(Sn—C—^1H)$ and the constituent, one-bond $^1J(Sn—^{13}C)$ and $^1J(^{13}C—^1H)$ coupling constants, but the correlation coefficient for the comparison between the two one-bond couplings, $^1J(Sn—^{13}C)$ and $^1J(^{13}C—^1H)$ is lower ($r = 0.872$). Changes in the couplings at the methyltin carbon bond tin-119 atoms are interpreted in terms of isovalent hybridization; a model based upon effective nuclear charges is tested with respect to both NMR coupling constants and ^{119}Sn Mössbauer Isomer shifts at tin and is invalidated. Proton and carbon-13 NMR chemical shift and coupling constant data are used to derive a Hammett σ-constant for the *para*-trimethyltin group of —0.14, and the significance of this value is discussed.

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Introduction

No satisfactory value of the Hammett σ-constant of the trimethyltin group is now available in the chemical literature. Estimates based upon the measured pK_a for *para*-trimethylstannylbenzoic acid of 1.051 ± 0.008 [3] give the σ-constant as 0.0 ± 0.1 [4]. Small errors are magnified in the derivation of values close to zero, and given a value identically zero, the question of whether the overall influence of the trimethyltin group is electron donating or withdrawing remains unanswered [5].

From the nuclear magnetic resonance technique we can derive data for neutral, ground state molecules of a very high precision. The use of Fourier transform methods allows more accuracy in the extrapolation to infinite dilution than previously possible. Aryltrimethyltin derivatives are ideal for a study of this type because of the variety of NMR data which can be brought to bear. We report in this paper ^1H chemical shift and coupling data for thirteen *meta-* and *para*-substituted aryltrimethyltin compounds. At this point in our studies we can summarize the ^1H and ^{13}C data to derive a Hammett σ-constant for the *para*-trimethyltin group.

Results

The methyltin proton chemical shifts for the thirteen *meta-* and *para*-substituted aryltrimethyltin derivatives studied (extrapolated to infinite dilution in CCl_4 solution) are shown in Table 1. These data were obtained at 100 MHz, and are listed with the exception of the trimethyltin group itself in order of increasing Hammett σ-constant. Some measurements at 60 MHz have been previously reported for phenyltrimethyltin [6,7] and certain of its derivatives [7—9].

The one-bond $|J(^{13}C—^1H|$ and the two-bond $|J(^{119}Sn—C—^1H)|$ coupling constants for the thirteen derivatives are shown in the same manner in Table 2.

TABLE 1

METHYL CHEMICAL SHIFTS IN $XC_6H_4Sn(CH_3)_3$ (± 0.1 Hz)^a

X	δ
p-$N(CH_3)_2$	21.5
p-OCH_3	24.3^b
p-OC_2H_5	24.0
p-CH_3	25.0^c
m-CH_3	26.0^d
H	27.3^e
p-F	27.7^f
m-OCH_3	27.1^g
p-Cl	28.1
p-Br	28.0^h
m-F	29.9^i
m-Cl	30.5
p-$Sn(CH_3)_3$	26.2^j

[a] Extrapolated to infinite dilution in CCl_4 relative to internal TMS in Hz. [b] Lit. 14.4 Hz at 60 MHz [7]. [c] Lit. 16.0 Hz [6], and 14.7 Hz at 60 MHz [7]. [d] Lit. 15.4 Hz at 60 MHz [7]. [e] Lit. 17.0 Hz [6], 16.0 Hz [7] and at 0.267 ppm [8] all at 60 MHz. [f] Lit. 16 Hz at 60 MHz [9]. [g] Lit. 16.2 Hz at 60 MHz [7]. [h] Lit. 16.3 Hz at 60 MHz [7]. [i] Lit. 17 Hz at 60 MHz [9]. [j] Lit. 15.6 Hz at 60 MHz [7].

TABLE 2

COUPLING CONSTANTS (±0.1 Hz) 30% in CCl_4

X	$\|^1J(^{13}C—^1H)\|$	$\|^2J(^{119}Sn—C—^1H)\|$
p-$N(CH_3)_2$	128.1	54.2
p-OCH_3	128.3	54.4[a]
p-OC_2H_5	128.2	54.5
p-CH_3	128.5	54.6[b]
m-CH_3	128.5	54.5[c]
H	128.6	54.6[d]
p-F	128.6	55.0[e]
m-OCH_3	128.5	54.7[f]
p-Cl	128.8	55.1
p-Br	128.8	55.1[g]
m-F	128.8	55.2[h]
m-Cl	129.0	55.2
p-$Sn(CH_3)_3$	128.4	54.6[i]

[a] Lit. 54.3 Hz [7]. [b] Lit. 54.3 Hz [6] and 54.4 Hz [7]. [c] Lit. 54.3 Hz [7]. [d] Lit. 54.6 Hz [6,7] and 54.7 Hz [8]. [e] Lit. 55.5 Hz [9]. [f] Lit. 55.3 Hz [7]. [g] Lit. 54.3 Hz [7]. [h] Lit. 55.5 Hz [9]. [i] Lit. 54.4 Hz [7].

Some data measured at 60 MHz have been previously reported for phenyltrimethyltin [6,7] and some of its derivatives, but no $^{13}C—^1H$ couplings have appeared before in the literature.

The methyltin proton chemical shifts and the $^{13}C—^1H$ and averaged $^{117,119}Sn—C—^1H$ coupling constant data are plotted against the Hammett σ-constants [10] for the corresponding substituents, and the regression analysis parameters for the linear relationship (the slope, ρ, in Hz/σ, intercept, C, in Hz and correlation coefficient, r), obtained for each case are listed for the chemical shifts in Table 3, and for the coupling constants in Table 4.

The chemical shift relationship meets the requirements stated by Miller et al. [11,12], that data for NMR correlations with Hammett constants be derived from measurements extrapolated to infinite dilution on a large number of representative compounds, giving a correlation coefficient above 0.95. The correlation coefficients for all twelve compounds are only slightly better than the r values for each of the *meta* and *para* series taken separately.

The coupling constant relationships also meet the requirements for number of compounds studied and correlation coefficient greater than 0.95 [11, 12]. In the coupling data the value for the *meta*-methoxyl deviates from the general trend, and the $|J(^{13}C—^1H)|$ and $|J(Sn—C—^1H)|$ correlation coefficients would increase to 0.976 and 0.973, respectively, for all compounds if this data point

TABLE 3

CHEMICAL SHIFT REGRESSION ANALYSIS PARAMETERS

	$\rho(Hz/\sigma)$[a]	C(Hz)[a]	r[b]	n[c]
All compounds	8.84	26.6	0.984	12
para-Derivatives	8.34	26.6	0.982	8
meta-Derivatives	8.84	26.7	0.981	5

[a] Parameters of the equation $\delta = \rho\sigma + C$. [b] Correlation coefficient. [c] Number of compounds.

TABLE 4

COUPLING CONSTANT REGRESSION ANALYSIS PARAMETERS

	ρ(Hz/ρ)[a]	C(Hz)[a]	r[b]	n[c]
$\|^1J(^{13}C—^1H)\|$ vs. σ				
All compounds	0.841	128.6	0.952	12
para-Derivatives	0.856	128.6	0.969	8
meta-Derivatives	0.972	128.5	0.907	5
$\|^2J(Sn—C—^1H)\|$[d] vs. σ				
All compounds	1.11	53.6	0.955	12
para-Derivatives	1.14	53.6	0.984	8
meta-Derivatives	1.53	53.4	0.974	5

[a] Parameters of the equation $J = \rho\sigma + C$. [b] Correlation coefficient. [c] Number of compounds. [d] Averaged values of tin-117, 119 coupling components were used.

were to be excluded. In addition, only marginal changes accrue from the use of differential coupling constants [2], $[J—J_H]/J$, based on J_H, the corresponding coupling in phenyltrimethyltin.

Discussion

Each of the three NMR parameters measured by the improved Fourier transform techniques employed here at 100 MHz produces a satisfactory correlation with the Hammett σ-constants, that is, with correlation coefficient, $r > 0.95$.

The ρ values calculated in this study from the methyltin proton chemical shift and $^{13}C—^1H$ coupling constant data can be compared to those for the tert-butyl, trimethylsilyl and trimethylgermyl series in Table 5 from the literature. Such comparison should be capable in principle of yielding the relative attenuation in the transmission of substituent effects, which, for the lower congeners of the fourth group are of particular interest because of the possibilities that π-interactions with the aromatic ring will make a contribution. This, together with the greater polarizability of the heavier elements of the group, would lead to the expectation that the ρ value should increase sharply after carbon in the series. Examination of Table 5, however, shows that this is clearly not the case, but that for the chemical shift data, the solvent effects are much larger than the small variations seen. Negative ρ values, for example, are obtained in benzene for series of trimethyl-silyl and -germyl compounds of —11.3 and —10.2, respectively [18,19], as well as for methyl-phosphorus, -arsenic and -sulfur derivatives [15]. While the coupling constant data would be expected to be relatively insensitive to such solvent effects, the values are apparently dependent upon which derivatives are included, as can be seen for the two silicon series studied in refs. 15 and 17. In addition, except for the carbon and tin cases, none of the previous studies resulted in correlations of greater than 0.9. Thus there is not sufficient difference among the ρ values of these series to justify conclusions regarding the relative ability to transmit substituent effects.

TABLE 5

COMPARATIVE METHYL PROTON CHEMICAL SHIFT AND $|^1J(^{13}C-^1H)|$ COUPLING CONSTANT REGRESSION ANALYSIS PARAMETERS FOR $(H_3C)_3EC_6H_4R$ AT 60 MHz in CCl_4

E	Chemical Shifts				Ref.	Coupling Constants			
	ρ(Hz/σ)[a]	C(Hz)[a]	r[b]	n[c]		ρ(Hz/σ)[a]	C(Hz)[a]	r[b]	n[c]
C	4.56	78.3	0.946	7	14	1.03[d]	125.6	0.928	8
	5.85	78.3	0.841	13	16				
Si	3.33[e,f]	24.3	0.369	16	17	1.28[e]	119.4	0.724	15
						1.58[g]	119.5	0.793	8
						1.16[h]	119.5	0.819	8
	3.83	14.4	0.923	9	15	0.130	119.2	0.150	8
						0.323[g]	119.2	0.752	7
						—0.870[h]	119.2	1.00	2
	5.86[i]	—71.0	0.933	6	16				
Ge	4.48	21.5	0.975	8	15	0.903	125.6	0.815	8
						1.03[g]	125.6	0.866	6
						0.089[h]	125.5	0.138	3
Sn	5.23	16.0	0.982	12	[j]	0.841	128.6	0.952	12
						0.856[g]	128.6	0.969	8
						0.972[h]	128.5	0.907	5

[a] Parameters of the equation $\delta = \rho\sigma + C$. [b] Correlation coefficient. [c] Number of compounds. [d] Same as for *para* only. [e] Excluding the *meta*- and *para*-nitro derivatives, the data for which were apparently used, but do not appear in ref. 17, which does not list regression analysis parameters for all 16 derivatives taken together. [f] Recorded in methylene chloride. [g] *para* only. [h] *meta* only. [i] Recorded with respect to cyclohexane. [j] This work. Chemical shift data from this study converted by 6/10 for comparison purposes.

The attenuation of the effect exerted by the *para*- and *meta*- substituents through the tin molecules themselves can, however, be examined with reference to Table 6 which compares the ρ values based upon coupling constants between pairs of nuclei. The magnitudes of these ρ values fall off by approximately one tenthfold per bond in the order $\rho[^{13}C(1)-Sn] > \rho[Sn-^{13}C] > \rho[^{13}C-^1H]$, presumably reflecting the attenuation of the substituent effect as it is propagated through this part of the molecules. This interpretation is also supported by ρ values derived from carbon-13 chemical shift data which decrease from 18.17 for C(1) to

TABLE 6

COMPARATIVE ρ VALUES DERIVED FROM COUPLING CONSTANT REGRESSION ANALYSIS FOR $(H_3C)_3SnC_6H_4R$

	ρ[a]		
	$|^1J(^{13}C(1)-Sn)|$[b]	$|^1J(Sn-^{13}C)|$[b]	$|^1J(^{13}C-^1H)|$
All derivatives	—80.62[c]	10.40[d]	0.841
para-only	—80.94[e]	10.85[f]	0.856
meta-only	—90.62[g]	17.28[h]	0.972

[a] Parameter of the equation $J = \rho\sigma + C$. [b] Data from ref. 2; averaged values of tin-117,119 coupling components were used. [c] $r = 0.991$; 12 compounds studied. [d] $r = 0.886$; 12 compounds studied. [e] $r = 0.995$; 8 compounds studied. [f] $r = 0.907$; 8 compounds studied. [g] $r = 0.984$; 5 compounds studied. [h] $r = 0.960$; 5 compounds studied.

—0.06 for the methylcarbon for the twelve substituted aryltrimethyltin derivatives discussed here [2].

The use of data for the coupling constant ${}^{2}J({}^{119}\mathrm{Sn{-}C{-}}{}^{1}\mathrm{H})$ in drawing inferences concerning structure and bonding in methyltin compounds is now very widespread, but assumptions regarding changes in *s*-character based upon idealized hybrids have little foundation in theory [20]. Changes in the two-bond tin—proton coupling, while easy to measure from the characteristic satellite patterns, may involve changes at the carbon as well as at the tin atom. Both the ${}^{1}J({}^{119}\mathrm{Sn{-}}{}^{13}\mathrm{C})$ and the ${}^{1}J({}^{13}\mathrm{C{-}}{}^{1}\mathrm{H})$ coupling constants must be known before the interpretation of the ${}^{2}J$ values in terms of *s*-character redistributions and structure can be carried out with confidence. Except for the methyltin halides [21], no such data for a representative number of compounds in which electron demand has been systematically varied have been published to date.

Regression analysis parameters derived from various combinations of the one- and two-bond coupling constant values measured in the thirteen substituted phenyltrimethyltin compounds studied are presented in Table 7. We have already published the analogous regression analysis data for the one-bond methyltin—carbon-13 values plotted against one another [2]. The correlation coefficients for the comparison of the two-bond, tin—proton coupling with each of the component one-bond, tin—carbon and carbon—proton couplings are greater than 0.95, and thus satisfactory, and the sign of the ρ values reverses when comparisons are drawn with the coupling between tin and the phenyl ring carbon to which it is attached [C(1)]. At least in this closely-related series of compounds interpretations from the tin-117, 119 proton satellite spectra alone could be employed, since a linear correlation with the constituent one-bond couplings is observed. The lines do not pass through the origin, however, 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 arrived at as a result of studies of $|{}^{1}J({}^{119}\mathrm{Sn{-}}{}^{13}\mathrm{C})|$ and $|{}^{2}J({}^{119}\mathrm{Sn{-}C{-}}{}^{1}\mathrm{H})|$ employing methyltin halides [21] and of $|{}^{2}J({}^{119}\mathrm{Sn{-}C{-}}{}^{1}\mathrm{H}|$ and $|{}^{3}J({}^{119}\mathrm{Sn{-}C{-}C{-}}{}^{1}\mathrm{H})|$ employing ethyltin compounds [22]. Further studies with other homologous series of compounds are needed before the question of the correct interpretation of the two-bond, tin—proton coupling constant in methyltin compounds is fully resolved.

The effect of substituent change in terms of electron density redistributions between the tin 5*s*- and 5*p*-orbitals has already been discussed on the basis of

TABLE 7

REGRESSION ANALYSIS PARAMETERS FOR COMPARISONS OF COUPLING CONSTANT DATA[a] INVOLVING THE METHYLTIN GROUP

	ρ(Hz/σ)	C(Hz)	r[b]	n[c]
Methyl $\lvert{}^{1}J(\mathrm{Sn{-}}{}^{13}\mathrm{C})\rvert$ vs. $\lvert{}^{2}J(\mathrm{Sn{-}C{-}}{}^{1}\mathrm{H})\rvert$	9.94	—190.7	0.959	13
Methyl $\lvert{}^{1}J(\mathrm{Sn{-}}{}^{13}\mathrm{C})\rvert$ vs. $\lvert{}^{1}J({}^{13}\mathrm{C{-}}{}^{1}\mathrm{H})\rvert$	11.9	—1183.2	0.872	13
$\lvert{}^{2}J(\mathrm{Sn{-}C{-}}{}^{1}\mathrm{H})\rvert$ vs. $\lvert{}^{1}J({}^{13}\mathrm{C{-}}{}^{1}\mathrm{H})\rvert$	1.25	— 107.9	0.959	13
$\lvert{}^{1}J(\mathrm{Sn{-}}{}^{13}\mathrm{C(1)})\rvert$ vs. $\lvert{}^{2}J(\mathrm{Sn{-}C{-}}{}^{1}\mathrm{H})\rvert$	—68.6	4136.7	0.976	13
$\lvert{}^{1}J(\mathrm{Sn{-}}{}^{13}\mathrm{C(1)})\rvert$ vs. $\lvert{}^{1}J({}^{13}\mathrm{C{-}}{}^{1}\mathrm{H})\rvert$	—90.1	12042.1	0.977	13

[a] Averaged values of the tin-117,119 coupling components were used. [b] Correlation coefficient. [c] Number of compounds.

the tin coupling data for both the C(1) and methyltin carbons in the series of compounds studied here. It was seen that as electron demand in the phenyl system increased, the $|^1J(^{119}Sn—^{13}C(1))|$ values decreased and the $|^1J(^{119}Sn—^{13}CH_3)|$ values increased corresponding to a concentration of tin 5*s*-character in the hybrid orbitals directed toward the methyl group carbon atoms [2]. In the present study we find a corresponding, but much smaller increase in $|^1J(^{13}C—^1H)|$ with increasing electron demand in the phenyl system as expected from the isovalent hybridization concept of Bent [23] applied to the electron redistributions between the carbon 2*s* and 2*p*-orbitals. Apparently the decreasing 2*s*-character of the carbon hybrid orbital directed toward the tin atom is more than offset by the increase in tin 5*s*-character in the resulting bond to give a net increase in $|^1J(^{119}Sn—^{13}C)|$ [2].

The model of Grant and Lichtman for $^1J(^{13}C—^1H)$ is based on changes in the effective nuclear charge [24]. If these changes at carbon or tin are important, then our explanation of the coupling constant data in terms of isovalent hybridization would be invalid. The model predicts an increase in $J(^{119}Sn—C—^1H)$ with an increase in effective nuclear charge at tin:

$$J(k) = \frac{\Delta_{ref}}{\Delta_{ref}} \left(\frac{N_k}{N_{ref}}\right)^2 \left(\frac{\alpha_k}{\alpha_{ref}}\right)^2 \left(\frac{Z_k}{Z_{ref}}\right)^3 J(\text{ref}) \qquad (1)$$

where $J(k)$ is the methyltin $^2J(^{119}Sn—C—^1H)$ coupling constant in the *k*th Sn—C—H bond, J(ref) is the same value in a reference compound, Δ is the average excitation energy, N is a bond normalization constant defined by Karplus and Grant [25], α^2 is directly proportional to the fractional *s*-character, and Z represents the effective nuclear charge appearing in the tin 5*s* orbital of the form $(Z_k/a_0)^{3/2}$ $(A + BZr + CZ^2r^2 + DZ^3r^3 + EZ^4r^4)e^{-Zr/5}$. The ratios Δ_{ref}/Δ_k and $(\alpha_k/\alpha_{ref})^2$ were assumed to be unity in their calculations. Thus an increase in effective nuclear charge will result in an increase in $J(^{119}Sn—C—^1H)$ and in a radial contraction of the tin 5*s*-orbital and a corresponding increase in $|\psi_s(0)|^2$.

The Isomer Shift from the ^{119}Sn Mössbauer spectra is related to the *s*-electron density at the tin nucleus, $|\psi_s(0)|^2$, as well [26], and the Isomer Shift, IS, can be substituted for Z^3 in eqn. 1:

$$J(k) = \frac{\Delta_{ref}}{\Delta_k} \left(\frac{N_k}{N_{ref}}\right)^2 \left(\frac{\alpha_k}{\alpha_{ref}}\right)^2 \frac{IS_k}{IS_{ref}} J(\text{ref}) \qquad (2)$$

The values of the Isomer Shifts for the thirteen substituted phenyltrimethyltin compounds studied here are all the same within experimental error, 1.28 ± 0.04 mm/s [27], and the interpretation of $J(^{119}Sn—C—^1H)$ values, or the component $J(^{119}Sn—^{13}C)$ and $J(^{13}C—^1H)$ values, based upon changes in effective nuclear charge at either carbon or tin, is clearly incorrect. Similar conclusions have been reached from studies of adducts of trimethyltin chloride [28].

The total electron densities at carbon atom positions can be inferred from the carbon-13 NMR chemical shifts, especially in aromatic systems [29]. The methyltin ^{13}C chemical shifts move upfield with increasing electron demand in the phenyl ring, signifying increased shielding and electron density at this site, opposite to, for example, the effect felt at C(1) [2]. The correlation coefficient for the inverse relationship with the Hammett σ-values for the methyltin carbon chemical shifts is poor, but improves for the *para*-substituted trimethylgermyl, silyl and tert-butyl derivatives ($r > 0.95$ for the latter two series) [30].

The electron densities can likewise be inferred from the carbon chemical shifts of the α-carbon in substituted tert-butylbenzenes, and excellent correlations are obtained with the Hammett σ-constants in *para*-substituted derivatives [30]. The same general relation is seen to hold for the tin-119 NMR chemical shifts measured for the thirteen derivatives studied here, but in this case the relationship is more complex [31].

The Hammett σ-constant of the *para*-trimethyltin group

One goal of the present study was to derive a reliable value of the Hammett σ-constant for the *para*-trimethyltin group, now lacking in the chemical literature. Our series of thirteen members is the most populated thus far studied, and we have collected NMR chemical shift and coupling constant data involving all the spin of one-half nuclei common to each member of the series. The required value can be produced from a statistical summary of these data, in which the regression analysis parameters for each parameter measured for the twelve substituted phenyltrimethyltin compounds vs.the Hammett σ-constant of each substituent group are used to derive a σ-value for the thirteenth, the *para*-trimethyltin group.

The results for twelve different NMR chemical shifts and coupling constants are shown in Table 8 along with the correlation coefficients for the relation of the twelve (all derivatives) or eight (*para*-derivatives only) compounds with corresponding Hammett σ-constants. These Hammett σ-constants lie in the range —0.038 to —0.22 with the exception of those values based on the carbon-13 chemical shift data for the methylcarbon and the phenylcarbon bearing the substituent, C(1). These two parameters, as can be seen by the very low values of r, do not correlate with the Hammett σ-constants, and we will exclude the derived σ-constants for the *para*-trimethyltin group from these sources from further discussion. For the remaining data, the differences between the Hammett σ-constants derived from consideration of all derivatives, or the *para*-derivatives only, is negligible, and so values from all twelve compounds will be used. In addition, the σ-constants from the parameters showing the smallest correlation coefficients, the methyltin $^1J(\text{Sn—}^{13}\text{C})$ coupling constants and the C(1) carbon-13 chemical shifts, are in the center of the range of values, and so need not be excluded.

The Hammett σ-constants derived from coupling constant values for all twelve compounds lie in the range —0.052 to —0.19 with a mean value of —0.142. The σ-constants derived from chemical shift values are —0.045 from the proton shifts, and —0.17 from the carbon-13 chemical shifts of the C(1) carbon of the phenyl group. Using the σ-constants from the *para*-derivatives only gives —0.038 and —0.23, respectively, with a mean value of —0.134. Given the limits of precision intrinsically associated with such derived parameters, we assign a value of —0.14 for the Hammett σ-constant for the *para*-trimethyltin group.

A Hammett σ-constant of small magnitude and negative sign agrees well with the known chemical and physical properties of trimethyltin-substituted compounds [32]. Electron release relative to hydrogen is to be expected on the

TABLE 8

DERIVED HAMMETT σ-CONSTANTS FOR THE *para*-$Sn(CH_3)_3$ GROUP[a]

	All derivatives	r^b	*para*-derivatives	r^c
Proton NMR data[d]				
A. Methyl chemical shifts	—0.045	0.984	—0.038	0.982
B. Methyl coupling constants				
$^{1}J(^{13}\mathrm{C}{-}^{1}\mathrm{H})$	—0.15	0.952	—0.16	0.969
$^{2}J(\mathrm{Sn}{-}\mathrm{C}{-}^{1}\mathrm{H})$	—0.19	0.955	—0.22	0.984
C. Differential coupling constants[e]				
$^{1}J(^{13}\mathrm{C}{-}^{1}\mathrm{H})$	—0.18	0.955	—0.20	0.074
$^{2}J(\mathrm{Sn}{-}\mathrm{C}{-}^{1}\mathrm{H})$	—0.16	0.946	—0.19	0.979
Carbon NMR data[f]				
A. Chemical shift				
Methyl	2.0	0.202	2.0	0.245
C(1)	0.17	0.900	0.23	0.902
C(x)[g]	0.35	0.249	0.017	0.522
B. Tin—carbon coupling constants				
Methyl $^{1}J(\mathrm{Sn}{-}^{13}\mathrm{C})$	—0.17	0.866	—0.21	0.907
Phenyl $^{1}J(\mathrm{Sn}{-}\mathrm{C}(1))$	—0.052	0.991	—0.062	0.995
C. Differential tin—carbon coupling constants[e]				
Methyl	—0.16	0.868	—0.20	0.909
Phenyl C(1)	—0.076	0.981	—0.071	0.992

[a] From appropriate regression analysis parameters, using data for the *para*-$Sn(CH_3)_3$ derivative. [b] Correlation coefficient; number of compounds = 12. [c] Correlation coefficient; number of compounds = 8. [d] This study. [e] Based on $[J-J(\mathrm{H})]/J$, where J is the averaged tin-117, tin-119 coupling to the particular atom listed and $J(\mathrm{H})$ is the corresponding averaged coupling in phenyltrimethyltin. [f] Ref. 2. [g] Substituent-bearing carbon atom [C(4) for *para*-, C(3) for *meta*-derivatives].

basis of the electronegativity of tin [33], but the precise ordering of electronegativity values in the fourth group below carbon is still the subject of controversy [32]. The Hammett σ-constant we assign is not as large as those for the *para*-tert-butyl group (—0.197) [10], or the *para*-methyl group (—0.17) [10], but is more negative than that listed for the *para*-trimethylsilyl group (—0.072) [10, 34]. All sources agree that tin is more electropositive than silicon [32,33], but the Hammett σ-constants thus far derived for the trimethylsilyl and germyl groups have been based on measurements of rate constants for various chemical reactions or ionization constants for substituted benzoic acids in various solvent systems. Substituent constants derived from chemical reaction will be valid only in the case that chemical reactivity is related to the electron density of the atom or group 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. Substituent constants derived from free energy measurements (pK_a, ΔG) on benzoic acid dissociation, on the other hand, may be based upon reactions which are controlled by entropy changes in the solvent system rather than factors involving the internal energies (enthalpies) of the molecules themselves [35].

The *para*-trimethylsilyl, germyl and stannyl substituted benzoic acids are all stronger than the corresponding tert-butyl acid in 60.1% W/W aqueous ethanol [3], but the greater acid strength of the silyl-derivative has been shown to be due to its having the highest positive ΔS^0 for ionization of any substituted benzoic acid thus far measured (its ionization is at the same time the most endothermic). No thermodynamic data are yet available for the germyl and stannyl acids. We recognize that the more electropositive tin may be a better σ-donor while at the same time reducing electron release by C—Sn hyperconjugative [36] or $(p \rightarrow d)$—π interactions.

Nuclear magnetic resonance parameters are also affected by certain contributions which are in origin purely nuclear, such as the gyromagnetic ratios, or magnetic, as for example, anisotropy and paramagnetic effects on screening upon which chemical behavior has no direct bearing, but NMR measurements do have the advantage of providing information on ground-state, neutral molecules. The Hammett σ-constant values for the trimethyl-silyl and -germyl groups should be reevaluated using NMR parameters.

Experimental

Preparation. The compounds studied were prepared as described in ref. 2.

NMR parameters. All NMR parameters were measured at 100 MHz on a modified Varian HA-100D spectrometer, equipped for cw (continuous wave), FFT (fast Fourier transform), and ^{19}F-lock operation. The Fourier mode was employed in all measurements. Data were collected and processed by a Digilab FTS/NMR-3 pulse and data system (standard 128K disc memory). Samples were contained in 5 mm O.D. tubes, which held coaxial inner cells with 2 inch 2 mm O.D. stems (Wilmad Glass Co., Inc., Buena, New Jersey) containing C_6F_6, the external-lock material.

Coupling constants were determined directly from Teletype print out, thereby eliminating the need for conventional side-banding techniques. The number of pulses ranged from 200—1000. In all cases, 16384 (16K) data points were collected with a sampling frequency of 1515 sec^{-1}, yielding a resolution of ca. 0.1 Hz.

Methyl chemical shifts were also obtained directly with a resolution of ± 0.1 Hz. The results from at least three concentrations below 1% (vol/vol or wt/vol) were extrapolated to infinite dilution. Ten pulses were collected for each concentration.

Solvents used were spectroquality grade CCl_4. Tetramethylsilane (TMS) was employed as an internal standard. Ambient probe temperature was ca. 39°.

Acknowledgement

Our work is supported by the National Science Foundation under Grant GP-16,544. We thank the M and T Chemical Company for the donation of organotin starting materials.

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