

THE SYNTHESIS AND ^{19}F NMR SPECTRA OF SOME DERIVATIVES OF (4-FLUOROPHENYL)DIMETHYLTIN

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SUMMARY

A number of (4-fluorophenyl)dimethyltin compounds and their carbon analogues have been prepared, and the fluorine chemical shifts for these compounds relative to fluorobenzene as an internal standard have been determined in cyclohexane, chloroform and pyridine. It has been shown that the electron-accepting capacity of the $\text{Sn}(\text{CH}_3)_2\text{X}$ substituents (where X is a heteroatom) increases in chloroform solution and decreases in pyridine solution relative to the value in cyclohexane, pyridine inhibiting transmission of electronic effects through the tin atom. Correlation between the ^{19}F chemical shifts and the σ_1 and $\Sigma\sigma^0$ values for the groups on the metal atom has been found, indicating that the electronic interactions between the substituents and the tin atom are mainly inductive in nature. The abilities of $\text{Sn}(\text{CH}_3)_2$ and $\text{C}(\text{CH}_3)_2$ bridging groups to transmit such electronic effects have been shown to be similar.

INTRODUCTION

In a previous communication¹ a study of the ^{19}F NMR spectra of some fluoroaryltin compounds was reported which indicated in agreement with previously reported data²⁻⁴ that the electronic interactions involving the tin-aromatic carbon bond in tetraaryltin compounds are mainly inductive and that the solvent susceptibility of electronic effect of the Ar_3Sn groups is practically zero. The present study has been undertaken in an attempt to elucidate how the nature of the substituent on the metal atom effects the electronic effect of the SnR_2X groups and its solvent susceptibility. In addition, it appeared of interest to compare the abilities of organotin bridging groups to transmit electronic effects with that of their carbon-containing analogues.

There appears to be no quantitative information available to date on the ability of bridging groups containing non-transition metals to transmit electronic effects, whereas the corresponding ability of C-, N-, O- and S-containing bridges has been studied rather extensively⁵⁻⁶. Probably the best method at present available for exploring this problem and comparing the transmission of electronic effects in the compounds of non-transition metals and their organic analogues is provided by ^{19}F NMR spectroscopy which has been used extensively by Taft and his co-workers⁷⁻⁹, the main advantages of this method being its high sensitivity and the possibility of studying rather labile compounds. Thus, recently, this method was used success-

fully to investigate the ability of some bridging groups in organic compounds of different types¹⁰⁻¹¹ to transmit electronic effects.

RESULTS AND DISCUSSION

In order to determine the influence of substituents at the metal atom upon the electronic effect of the SnR_2X groups and to compare the ability of $-\text{SnR}_2-$ and $-\text{CR}_2-$ bridges, to transmit this effect, the following (4-fluorophenyl)dimethyltin compounds and their carbon analogues have been prepared: $4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{X}$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OH}, \text{C}_6\text{H}_5\text{O}, \text{CH}_3\text{COO}, \text{C}_6\text{H}_5\text{S}, \text{C}_6\text{H}_5, 3\text{-ClC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 3\text{-CH}_3\text{OC}_6\text{H}_4, 4\text{-CH}_3\text{OC}_6\text{H}_4$ and $3,4,5\text{-Cl}_3\text{C}_6\text{H}_2$; $4\text{-FC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{Y}$, where $\text{Y} = \text{C}_6\text{H}_5, 4\text{-CH}_3\text{OC}_6\text{H}_4$ and $3,4,5\text{-Cl}_3\text{C}_6\text{H}_2$.

The fluorine chemical shifts of all the above compounds relative to fluorobenzene as an internal standard have been determined in cyclohexane, chloroform and pyridine. Cyclohexane was taken as an example of a very inert solvent, chloroform as a solvent capable of forming hydrogen bonds with the anionic part of the organometallic substituents¹²⁻¹³ and pyridine as a strongly coordinating solvent. Consideration of the results obtained (Table 1) allows the following observations to be made.

The solvent susceptibility of electronic effect of an organotin substituent (which as a first approximation may be represented by the change in the fluorine chemical shift in the corresponding compound on replacing cyclohexane by a coordinating or hydrogen-bond forming solvent) is substantially dependent on the nature of the group attached to the metal atom. Thus, substituents of the type $(\text{CH}_3)_3\text{Sn}$ and $\text{Ar}(\text{CH}_3)_2\text{Sn}$ have a similar inability to transmit such effects in the same way as the $(\text{C}_6\text{H}_5)_3\text{Sn}$ group studied previously¹. With these substituents the changes in the fluorine chemical shift in the corresponding compounds on replacing cyclohexane by pyridine or chloroform are, as a rule, very similar to the experimental error involved. Somewhat larger changes in the fluorine chemical shifts on replacing cyclohexane by chloroform are observed with $\text{Ar}(\text{CH}_3)_2\text{Sn}$ groups probably because of hydrogen-bond formation between the solvent and the aromatic ring or a substituent attached to the latter. On the other hand, the considerable decrease in electron-withdrawing ability of the $3,4,5\text{-Cl}_3\text{C}_6\text{H}_2(\text{CH}_3)_2\text{Sn}$ group when cyclohexane is replaced by pyridine as the solvent is apparently due to coordination between the solvent and the metal atom. This is supported by the absence of a solvent effect with the corresponding carbon analogue.

A large increase in the solvent susceptibility of electronic effect of the organotin substituent is observed if one of the valence orbitals of the metal atom is involved in linkage to a heteroatom. Under these circumstances hydrogen-bond formation between the solvent and the anionic part of the molecule, *i.e.* $4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{X} \cdots \text{HCCl}_3$, or coordination between the solvent and the tin atom, *i.e.* $4\text{-FC}_6\text{H}_4(\text{CH}_3)_2\text{-NC}_5\text{H}_5$, leads to a pronounced increase or decrease respectively in the electron-accepting capacity of the organometallic substituent. The influence of hydrogen bonding with the solvent upon the electronic effect of the organotin substituent does not always run parallel to the electron-withdrawing capacity of the X group. Thus, the

change in the fluorine chemical shift on replacing cyclohexane by chloroform as a solvent is smaller for (4-fluorophenyl)dimethyltin phenoxide than for the corresponding chloride, despite the fact that because of fluorine shielding in cyclohexane solution the $\text{Sn}(\text{CH}_3)_2\text{OC}_6\text{H}_5$ group should be more electron-accepting than $\text{Sn}(\text{CH}_3)_2\text{Cl}$ and the $\text{Sn}-\text{O}$ bond should be more polar than $\text{Sn}-\text{Cl}$. In contrast, with halogen-containing substituents the effect of hydrogen bonding is reduced on going from the chloride to the iodide, thus changing parallel to the electron-withdrawing capacity of these organotin groups. The observed increase in fluorine shielding on replacing cyclohexane by pyridine is dependent on the nature of the halogen atom attached to the metal atom and follows the sequence $\text{I} < \text{Br} < \text{Cl}$.

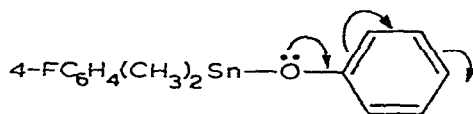
TABLE 1

^{19}F CHEMICAL SHIFTS RELATIVE TO INTERNAL FLUOROBENZENE (in ppm)

Compound	Solvent		
	C_6H_{12}	CHCl_3	$\text{C}_5\text{H}_5\text{N}$
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{I}$	-2.50	-2.97	-1.68
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{Br}$	-2.66	-3.24	-1.54
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{Cl}$	-2.75	-3.33	-1.13
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{OC}_6\text{H}_5$	-3.09	-3.46	-1.54
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{OCOCH}_3$	^a	-2.84	-0.90
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{SC}_6\text{H}_5$	-1.74	-2.05	-1.49
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_3$	0.30	0.12	0.14
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{C}_6\text{H}_5$	-0.30	-0.54	-0.44
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{OCH}_3\text{-4}$	0.00	-0.38	-0.27
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{OCH}_3\text{-3}$	-0.30	-0.62	-0.57
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{F-4}$	-0.64	-0.75	-1.22
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Cl-4}$	-0.87	-0.88	-0.68
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{Cl-3}$	-0.83	-0.95	-0.94
$4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{C}_6\text{H}_2\text{Cl}_3\text{-3,4,5}$	-1.79	-1.68	-1.26
$4\text{-FC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_5$	4.65	4.86	4.27
$4\text{-FC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{OCH}_3\text{-4}$	5.25	5.06	4.61
$4\text{-FC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_2\text{Cl}_3\text{-3,4,5}$	3.00	3.43	3.09

^a Solubility problems.

For the $\text{Sn}(\text{CH}_3)_2\text{OC}_6\text{H}_5$ group, the observed increase in fluorine shielding is slightly smaller than that expected on the basis of its electron-accepting capacity alone. In this case it is possible that the anomalously low solvent susceptibility of electronic effect for this substituent may be associated both with the delocalization of the partial negative charge on the oxygen atom on to the aromatic ring, i.e.



and with steric hindrance arising from free rotation of the $\text{C}_6\text{H}_5\text{O}$ group around the $\text{Sn}-\text{O}$ bond limiting the approach of the solvent to the oxygen and metal atoms.

As may be seen from the data recorded in Table 1, substitution of sulphur for oxygen in the $\text{Sn}(\text{CH}_3)_2\text{OC}_6\text{H}_5$ group leads to a pronounced decrease in the solvent susceptibility of electronic effect of the organotin substituent, which is consistent with the smaller electronegativity of the sulphur atom relative to oxygen. The observation that the introduction of electron-withdrawing substituents at the metal atom results in the enhancement of its coordinating ability and gives rise to a considerable solvent susceptibility of electronic effect of the corresponding organotin substituents is evidently connected with the increase in the partial positive charge on tin and the resulting lowering of the energy of its vacant orbitals¹⁴. These factors facilitate sp^3d -hybridization of the tin orbitals on solvation.

Turning to a consideration of the influence of the groups attached to the metal atom upon the electronic effect of the organotin substituents, it should be remembered that according to some literature data¹⁻⁴ electronic interactions through the tin-aromatic carbon bond are mainly inductive in nature. Thus it may be expected that the influence of substituents at the metal atom upon the electronic effect of $\text{Sn}(\text{CH}_3)_2\text{X}$ groups would be reflected by the σ_I values of these substituents provided that the interactions across the Sn-X bonds are also inductive. On plotting the fluorine chemical shifts in the model compounds: $4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{X}$ against the σ_I values of the substituents attached to the metal atom, the latter either taken from Charton's compilation¹⁵ or calculated using Taft's method⁷, a fairly good linear correlation is observed between these parameters in cyclohexane and chloroform solutions (Figs. 1-2). The straight lines obtained may be described mathematically by the correlation equation:

$$Y = a + bX$$

the corresponding parameters being listed in Table 2. Such agreement also shows that hydrogen-bond formation between the solvent and the substituent attached to the tin atom does not appreciably affect the electronic interactions in the Sn-X bond.

TABLE 2

PARAMETERS OF CORRELATION EQUATIONS^a ($Y = a + bX$)

System	Solvent	X	Y	n	a	b	r	S	S _a	S _b
4-FC ₆ H ₄ Sn(CH ₃) ₂ R	C ₆ H ₁₂	$\sigma_I(\text{Ch})$	δ_F	7	0.10	-6.56	0.959	0.343	0.246	0.717
4-FC ₆ H ₄ Sn(CH ₃) ₂ R	CHCl ₃	$\sigma_I(\text{Ch})$	δ_F	7	-0.04	-7.48	0.972	0.315	0.225	0.657
4-FC ₆ H ₄ Sn(CH ₃) ₂ R	C ₅ H ₅ N	$\sigma_I(\text{Ch})$	δ_F	7	-0.15	-3.27	0.851	0.333	0.238	0.695
4-FC ₆ H ₄ Sn(CH ₃) ₂ R	C ₆ H ₁₂	$\sigma_I(\text{T})$	δ_F	7	-0.14	-6.18	0.928	0.455	0.302	0.916
4-FC ₆ H ₄ Sn(CH ₃) ₂ R	CHCl ₃	$\sigma_I(\text{T})$	δ_F	8	-0.41	-6.97	0.928	0.475	0.308	0.957
4-FC ₆ H ₄ Sn(CH ₃) ₂ R	C ₅ H ₅ N	$\sigma_I(\text{T})$	δ_F	8	-0.23	-3.10	0.858	0.308	0.200	0.621
4-FC ₆ H ₄ Sn(CH ₃) ₂ Ar	CHCl ₃	$\Sigma\sigma^0$	δ_F	7	-0.55	-1.12	0.999	0.015	0.004	0.016
4-FC ₆ H ₄ C(CH ₃) ₂ R (I)	C ₆ H ₁₂	$\delta_F(\text{I})$	$\delta_F(\text{II})$	4	-4.19	0.812	0.997	0.099	0.238	0.051
4-FC ₆ H ₄ Sn(CH ₃) ₂ R (II)		$\delta_F(\text{II})$								

^a $\sigma_I(\text{Ch})$ =inductive parameter of the substituent according to Charton's data¹⁵; $\sigma_I(\text{T})$ =inductive parameter of substituent according to Taft's data⁷; n=number of compounds in the system; r=correlation coefficient; S=standard error of the estimate; S_a=standard error of the coefficient a; S_b=standard error of the coefficient b; CL=confidence level for significance of correlation.

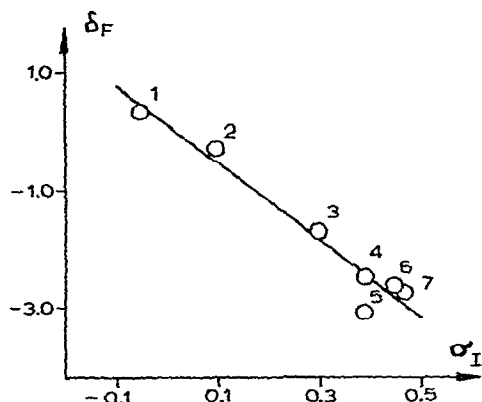


Fig. 1. Plot of the ^{19}F chemical shifts for 4- $\text{FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{R}$ in C_6H_{12} versus the inductive parameters (Charton) of the substituents R: 1, CH_3 ; 2, C_6H_5 ; 3, $\text{C}_6\text{H}_5\text{S}$; 4, I; 5, $\text{C}_6\text{H}_5\text{O}$; 6, Br; 7, Cl.

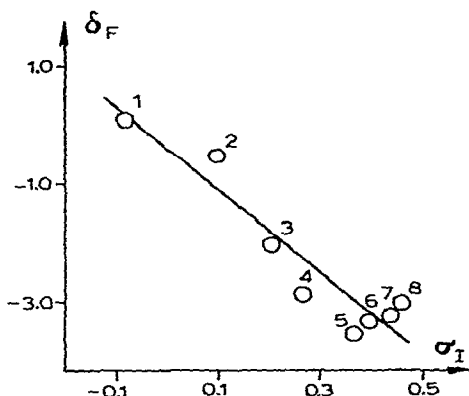


Fig. 2. Plot of the ^{19}F chemical shifts for 4- $\text{FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{R}$ in CHCl_3 versus the inductive parameters (Taft) of the substituents R: 1, CH_3 ; 2, C_6H_5 ; 3, $\text{C}_6\text{H}_5\text{S}$; 4, CH_3COO ; 5, $\text{C}_6\text{H}_5\text{O}$; 6, Cl; 7, Br; 8, I.

However, the corresponding correlations in pyridine solutions are much less satisfactory although remaining statistically significant. The decrease in the slope in moving from cyclohexane and chloroform to pyridine as a solvent indicates that in a coordinating solvent inhibition of the transmission of electronic effects through the metal atom is brought about by enhanced metal solvation, thus compensating for the effect of electron-attracting substituents.

The existence of a good correlation between the fluorine chemical shifts in the model compounds studied and the inductive parameters of the X substituents shows that the interaction of these substituents with the metal atom occurs mainly by an inductive mechanism. On the other hand, the relatively low value of the correlation coefficient, the perceptible scattering of points about the straight line and the fact that the $\text{Sn}(\text{CH}_3)_2\text{OC}_6\text{H}_5$ group is more electron-withdrawing in comparison with the halogen-containing organotin substituents suggest that additional electronic effects arising from d_π - p_π conjugation in the tin-element bonds may play some role in determining the magnitude of the fluorine shielding.

As may be seen from Table 2, the relationship between the fluorine chemical shifts for derivatives of (4-fluorophenyl)dimethyltin and Charton's inductive parameters is slightly better than that involving σ_I values calculated by Taft's method. At present it appears that a consideration of more subtle differences in the interaction of various substituents with the tin atom is not possible. Apparently, in order to obtain a more detailed understanding of the specificity of electronic interactions across the tin-heteroatom bond in comparison with those acting across aliphatic carbon-heteroatom bonds in the ground state it is necessary to compare the appropriate structurally similar model systems using a sufficiently sensitive physical technique rather than attempt to correlate parameters for a given system with σ_I values for substituents attached to the metal atom derived from reactivity data and/or physical measurements involving some other systems. If the physical technique employed is ^{19}F NMR spectroscopy, the appropriate model systems could be 4- $\text{FC}_6\text{H}_4\text{SnR}_2\text{X}$ and

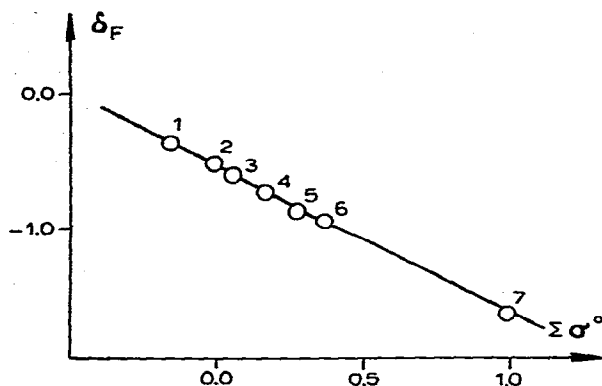


Fig. 3. Plot of the ^{19}F chemical shifts for $4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{Ar}$ in CHCl_3 versus the $\Sigma\sigma^0$ values for the substituted phenyl groups: 1, 4- $\text{CH}_3\text{OC}_6\text{H}_4$; 2, C_6H_5 ; 3, 3- $\text{CH}_3\text{OC}_6\text{H}_4$; 4, 4- FC_6H_4 ; 5, 4- ClC_6H_4 ; 6, 3- ClC_6H_4 ; 7, 3,4,5- $\text{Cl}_3\text{C}_6\text{H}_2$.

$4\text{-FC}_6\text{H}_4\text{CR}_2\text{X}$. In addition, it has been found in the present investigation that for the system $4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{Ar}$, where the variable substituent on the tin atom is a substituted phenyl radical, an excellent correlation is observed between the fluorine chemical shift and the $\Sigma\sigma^0$ value for the corresponding aryl group (Fig. 3, Table 2) despite the fact that the range of fluorine chemical shifts observed is only slightly smaller than in the system $4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{X}$. From the slope of the regression line, it follows that the ability of the $\text{Sn}(\text{CH}_3)_2$ bridging group to transmit electronic effects is intermediate between that of the $-\text{CH}=\text{CH}-$ and $-\text{CH}_2\text{CH}_2-$ groups¹⁰. The existence of the good correlation mentioned above may be associated with the fact that the relative contributions from various electronic interactions occurring in the tin-substituent bond remain constant within a given system involving only substituted aryl groups attached to the tin atom. However, with the more extended system $4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{X}$, where the metal atom is bonded to carbon in different hybridization states as well as to various heteroatoms, this situation does not occur. In this case the character of the electronic interactions between the substituent and the tin atom may change to a greater extent on going from one substituent to another due to varying contributions from the possible effects of $d_\pi-p_\pi$ and $d_\pi-d_\pi$ conjugation.

The confidence limits for the slope of the regression line are considerably less for the system $4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{Ar}$ than for the system $4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{X}$, suggesting that, in general, the model systems $4\text{-FC}_6\text{H}_4\text{MR}_n\text{Ar}_m$ should be most suitable for comparing the transmission of electronic effects through bridging groups containing non-transition metals or other elements. This is again connected with the fact that the relative contributions from possible $p_\pi-p_\pi$, $d_\pi-p_\pi$ and $d_\pi-d_\pi$ conjugation effects in the bonds between a non-transition metal atom and a heteroatom will depend on the nature of both atoms and for different metals may not change to the same extent for a particular substituent attached to one heteroatom as when attached to another heteroatom. In contrast, however, for the particular systems discussed above the relative magnitude of the major contribution arising from the inductive effect in relation to the less important contributions from the various types of conjugation will remain approximately constant as the nature of the substituted aryl groups is changed within each system.

TABLE 3

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF DERIVATIVES OF (4-FLUOROPHENYL)DIMETHYLTIN AND THEIR CARBON ANALOGUES

Compound	Yield (%)	M.p. (°C)	B.p. (°C/mmHg)	n_D^{20}	Analysis found (calcd.) (%)	
					C	H
4-FC ₆ H ₄ Sn(CH ₃) ₂ I	77		119/3	1.6057	26.48 (25.90)	2.60 (2.69)
4-FC ₆ H ₄ Sn(CH ₃) ₂ Br	93		100/3	1.5736	30.28 (29.62)	3.06 (3.09)
4-FC ₆ H ₄ Sn(CH ₃) ₂ Cl	90	34	106/3		34.61 (34.28)	3.51 (3.57)
4-FC ₆ H ₄ Sn(CH ₃) ₂ OH	85	84			36.76 (36.78)	4.08 (4.25)
4-FC ₆ H ₄ Sn(CH ₃) ₂ OC ₆ H ₅	83		154/3	1.5820	50.08 (49.85)	4.36 (4.43)
4-FC ₆ H ₄ Sn(CH ₃) ₂ OCOCH ₃	66	168			39.74 (39.60)	4.22 (4.29)
4-FC ₆ H ₄ Sn(CH ₃) ₂ SC ₆ H ₅	91		154/4		47.82 (47.56)	3.91 (4.26)
4-FC ₆ H ₄ Sn(CH ₃) ₂ C ₆ H ₅	63		124/3	1.5765	52.47 (52.34)	4.73 (4.67)
4-FC ₆ H ₄ Sn(CH ₃) ₂ C ₆ H ₄ OCH ₃ -4	64		155/3	1.5781	51.47 (51.25)	4.92 (4.84)
4-FC ₆ H ₄ Sn(CH ₃) ₂ C ₆ H ₄ OCH ₃ -3	71		156/3	1.5739	51.44 (51.25)	4.73 (4.84)
4-FC ₆ H ₄ Sn(CH ₃) ₂ C ₆ H ₄ Cl-4	70		142/2	1.5865	47.65 (47.19)	3.89 (3.93)
4-FC ₆ H ₄ Sn(CH ₃) ₂ C ₆ H ₄ Cl-3	76		143/2	1.5861	47.24 (47.19)	3.92 (3.93)
4-FCH ₄ Sn(CH ₃) ₂ C ₆ H ₂ Cl ₃ -3,4,5	99	87			39.34 (39.57)	2.84 (2.83)
4-FC ₆ H ₄ (CH ₃) ₂ C ₆ H ₅	44	73	130/4		83.94 (84.11)	6.89 (7.00)
4-FC ₆ H ₄ C(CH ₃) ₂ C ₆ H ₄ OCH ₃ -4	73		174/6	1.5565	78.79 (78.69)	7.16 (6.96)
4-FC ₆ H ₄ C(CH ₃) ₂ C ₆ H ₂ Cl ₃ -3,4,5	69	68	140/5		56.46 (56.64)	3.82 (3.77)

When the predominantly inductive nature of the electronic interactions occurring in the tin–aromatic carbon bond is taken into account, it might be expected that the relative contributions arising from the various electronic interactions in the substituent–metal bond would remain essentially constant in the system 4-FC₆H₄Sn(CH₃)₂R, where R is an alkyl or aryl group. For this reason, a comparison has been made between this system and the analogous system involving a carbon-containing bridging group, *i.e.* 4-FC₆H₄C(CH₃)₂R. In fact, a good linear correlation was observed between the fluorine chemical shifts in both systems (Fig 4, Table 2), the slope of the straight line obtained being equal to 0.812 with 95% confidence limits of 1.030 and 0.594, the small number of points involved in the plot unfortunately leading to the

rather wide confidence limits observed. On the basis of the data obtained it is possible to suggest tentatively that as a first approximation the relative capacities of the $-\text{Sn}(\text{CH}_3)_2-$ and $-\text{C}(\text{CH}_3)_2-$ bridging groups for relaying electronic effects are not all that different. A more detailed study of the $\text{Ar}_3\text{SnC}_6\text{H}_4\text{F}-4$ and $\text{Ar}_3\text{CC}_6\text{H}_4\text{F}-4$ systems, which is now in progress should enable a more reliable quantitative comparison to be made of the transmitting abilities of the $\text{Sn}-\text{C}_{\text{Ar}}$ and $\text{C}-\text{C}_{\text{Ar}}$ bonds.

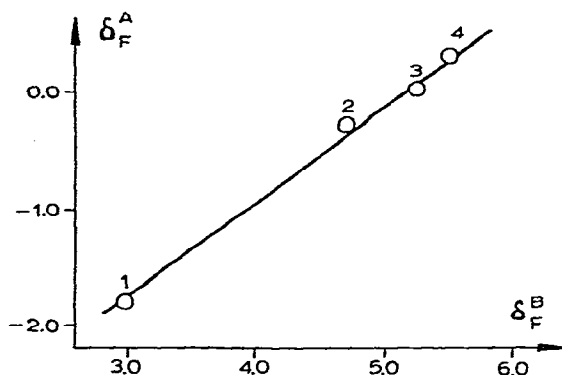


Fig. 4. Plot of the ^{19}F chemical shifts for $4\text{-FC}_6\text{H}_4\text{Sn}(\text{CH}_3)_2\text{R}$ in C_6H_{12} (δ_F^A) versus those for $4\text{-FC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{R}$ in the same solvent (δ_F^B): 1, 3,4,5- $\text{Cl}_3\text{C}_6\text{H}_2$; 2, C_6H_5 ; 3, 4- $\text{CH}_3\text{OC}_6\text{H}_4$; 4, CH_3 .

During the present study it was observed that the fluorine resonance in organotin compounds is shifted several ppm downfield relative to their carbon analogues. This fact could be of considerable interest in comparing the electronic effects of tin- and carbon-containing substituents. Thus according to these observations, the organotin substituents appear to be more electron-withdrawing than might be expected on the basis of the electronegativities of tin and carbon¹⁶. This anomalous behaviour cannot be explained in terms of conjugation involving the π -electrons of the aromatic ring and the vacant tin orbitals because this effect is quite small¹⁻⁴ and because a similar situation, although involving a smaller difference between the tin and carbon substituents, is encountered in a comparison of systems containing $(\text{CH}_3)_3\text{Sn}$ and $(\text{CH}_3)_3\text{C}$ groups in the *meta* position relative to the fluorine indicator atom^{2,17}.

The observed behaviour may be attributable to the difference in the extent of the interaction between the electron pairs of the $\text{Sn}-\text{CH}_3$ and $\text{C}-\text{CH}_3$ bonds and the electrons of the aromatic ring. With *meta* substituents, a stronger purely electrostatic through-space interaction¹⁸ may be operative between the electrons of the $\text{C}-\text{C}$ bonds and those of the aromatic ring, whereas with *para* substituents the above effect may be even greater because of σ, π -conjugation between the $\text{C}-\text{C}$ bonds and the ring¹⁹. The relatively weaker interactions of both these types observed with organotin groups are apparently attributable to the greater size and greater diffuseness of the tin orbitals in comparison with those of carbon. Because of the above factors, organotin groups in bonding to an aromatic ring may become less electron-donating than their carbon analogues, despite the greater polarization of the tin-aromatic carbon bond (as $\text{Sn} \rightarrow \text{C}$) in comparison with the bond between aliphatic and aromatic carbon atoms.

EXPERIMENTAL

General

The ^{19}F NMR spectra were recorded at 34° on a Hitachi-Perkin-Elmer R-20 spectrometer operating at 56.4 MHz. All measurements were performed on solutions of concentration not greater than $0.2 \text{ mol} \cdot \text{l}^{-1}$. The use of the substitution method for the determination of fluorine chemical shifts has been described elsewhere²⁰. The solvents were purified and dried by conventional methods. Cyclohexane was distilled over metallic sodium and chloroform over phosphorus pentoxide. Pyridine was distilled over potassium hydroxide and dried over molecular sieves.

Derivatives of (4-fluorophenyl)dimethyltin were prepared using the known compound bis(4-fluorophenyl)dimethyltin² as a starting material and converting it into (4-fluorophenyl)dimethyltin iodide by the action of iodine. Reactions of this compound with Grignard reagents enabled compounds with aryl substituents on the metal atom to be obtained. The action of KOH upon (4-fluorophenyl)dimethyltin iodide gave the corresponding hydroxide which through exchange reactions yielded derivatives of (4-fluorophenyl)dimethyltin with anionic groups attached to the tin atom. (4-Fluorophenyl)trimethyltin was obtained using the procedure previously reported²¹.

The fluorine chemical shifts for 4-fluoro-*tert*-butylbenzene were taken from the literature¹⁷. The σ_1 values for the I and $\text{C}_6\text{H}_5\text{S}$ substituents, calculated according to Taft's procedure⁷, were evaluated from the fluorine chemical shifts for 3-fluoroiodobenzene and (3-fluorophenyl)phenyl sulphide in chloroform solution. The former compound was prepared by the reported procedure²², the latter being obtained by the interaction of 3-fluorophenyldiazonium chloride with sodium thiophenoxide. 2-Aryl-2-(4-fluorophenyl)propanes were prepared by condensation of the corresponding carbinols with benzene or its derivatives.

The physical properties and analytical data for the compounds of (4-fluorophenyl)dimethyltin and their carbon analogues not reported previously are given in Table 3. The preparations of the various new compounds investigated in this study are described below.

(4-Fluorophenyl)dimethyltin iodide

To a solution of 5.0 g (15 mmol) of di(4-fluorophenyl)dimethyltin² in 30 ml of dry ether was added 3.7 g (14.5 mmol) of powdered iodine with stirring. The ether boiled gently and the iodine colour disappeared. After stirring at room temperature for 2 h, the solvent was removed and the residue distilled under reduced pressure yielding 4.3 g (77%) of a colourless oil.

(4-Fluorophenyl)dimethyltin hydroxide

A solution of 1.85 g (5 mmol) of (4-fluorophenyl)dimethyltin iodide in 10 ml of ether was shaken with a solution consisting of 0.6 g of potassium hydroxide in 2 ml of water. The white precipitate which formed was filtered, washed several times with water, recrystallized from water and dried *in vacuo* over sodium hydroxide when 1.1 g (85%) of colourless crystals was obtained.

(4-Fluorophenyl)dimethyltin bromide

A suspension of 1.3 g (5 mmol) of (4-fluorophenyl)dimethyltin hydroxide in

10 ml of ether was shaken in a separating funnel with 0.8 ml of 48 % hydrobromic acid. The ether layer was separated after dissolution of the hydroxide, washed with 2 ml of water, dried over Na_2SO_4 and the solvent removed. Distillation of the residue under reduced pressure gave 1.6 g (93 %) of a colourless oil. (4-Fluorophenyl)dimethyltin chloride was obtained in a similar fashion.

(4-Fluorophenyl)dimethyltin acetate

A suspension of 1.0 g (4 mmol) of (4-fluorophenyl)dimethyltin hydroxide in 10 ml of ether was shaken with 0.3 ml of acetic acid. The resulting solid was filtered and recrystallized from benzene, yielding 0.68 g (66 %) of colourless crystals.

(4-Fluorophenyl)dimethyltin phenoxide

A solution of 0.48 g (5 mmol) of phenol in 10 ml of dry benzene was added to a solution of 1.3 g (5 mmol) of (4-fluorophenyl)dimethyltin hydroxide in 50 ml of boiling benzene. After cooling, the resulting solution was dried over Na_2SO_4 , the solvent removed by distillation and the residue distilled *in vacuo* when 1.4 g (83 %) of a colourless oil was obtained.

(4-Fluorophenyl)dimethyltin thiophenoxide

To a solution of sodium thiophenoxide prepared from 0.12 g of sodium and 0.55 g (5 mmol) of thiophenol in 5 ml of methanol was added 1.85 g (5 mmol) of (4-fluorophenyl)dimethyltin iodide in 10 ml of the same solvent. After evaporation of the solvent, the residue was treated with water and ether. The ether layer was separated, washed with water and dried over Na_2SO_4 . The solvent was removed and the residue distilled under reduced pressure, yielding 1.6 g (91 %) of a colourless oil.

Phenyl(4-fluorophenyl)dimethyltin

To a Grignard reagent prepared from 3.14 g (20 mmol) of bromobenzene and 0.49 g of magnesium turnings in 15 ml of dry ether was added, with stirring, a solution of 3.7 g (10 mmol) of (4-fluorophenyl)dimethyltin iodide in 10 ml of the same solvent. After refluxing for 2 h, the reaction mixture was treated with an aqueous solution of NH_4Cl , the ether layer separated, washed with an aqueous solution of KF and dried over CaCl_2 . The solvent was removed and the residue distilled *in vacuo* affording 2.0 g (63 %) of a colourless oil.

3,4,5-Trichlorobromobenzene

A suspension of 24.6 g (0.1 mol) of 2,6-dichloro-4-bromaniline²³ in 200 ml of concentrated hydrochloric acid was diazotized with stirring and cooling to 0–10° by addition of 7.7 g (0.11 mol) of NaNO_2 in 20 ml of water. After addition of NaNO_2 was complete, the reaction mixture was stirred for 2 h at the same temperature and the filtered diazo solution was added to a boiling solution of 9.9 g of CuCl in 150 ml of concentrated hydrochloric acid. After evolution of nitrogen had ceased, the reaction product was steam-distilled and recrystallized from ethanol when 25.0 g (96 %) of colourless crystals of m.p. 56° was obtained, (lit.²⁴ m.p. 58°).

(4-Fluorophenyl)(3,4,5-trichlorophenyl)dimethyltin

To a solution of a Grignard reagent prepared from 2.0 g (8 mmol) of 3,4,5-trichlorobromobenzene and 0.19 g of magnesium in 15 ml of dry ether was added a

solution of 2.6 g (7 mmol) of (4-fluorophenyl)dimethyltin iodide in 5 ml of the same solvent. After refluxing for 2 h, the reaction mixture was decomposed with an aqueous solution of NH_4Cl , the ether layer separated, washed with a solution of KF , dried over CaCl_2 and the solvent evaporated. The crystalline substance obtained was recrystallized from petroleum ether with charcoal.

2-(3,4,5-Trichlorophenyl)propan-2-ol

To a Grignard reagent prepared from 3.1 g (12 mmol) of 3,4,5-trichlorobromobenzene and 0.37 g of magnesium in 10 ml of dry ether was added dropwise with stirring and cooling with ice water a solution consisting of 0.87 g (15 mmol) of acetone in 5 ml of ether. After refluxing for 2 h, the reaction mixture was decomposed with an aqueous solution of NH_4Cl , the ether layer separated, dried over Na_2SO_4 and the solvent removed. Distillation of the residue under reduced pressure gave 1.9 g (66%) of a colourless oil with b.p. $130^\circ/4$ mmHg, which crystallized on standing. Recrystallization from petroleum ether afforded colourless crystals with m.p. $75\text{--}76^\circ$. (Found: C, 44.96; H, 3.98. $\text{C}_9\text{H}_9\text{Cl}_3\text{O}$ calcd.: C, 45.09; H, 3.75%.)

2-Phenyl-2-(4-fluorophenyl)propane

To a suspension of 2.7 g (20 mmol) of AlCl_3 in 10 ml of benzene was added dropwise with stirring and cooling to 10° a solution consisting of 4.6 g (30 mmol) of 2-(4-fluorophenyl)propan-2-ol²⁵ in 10 ml of benzene. The reaction mixture was left overnight and then decomposed with ice and dilute hydrochloric acid. The organic layer was separated, washed with water, dried over Na_2SO_4 and the solvent removed. The residue was distilled *in vacuo* yielding 5.0 g of a colourless oil with b.p. $130/4$ mmHg, which crystallized partially on standing in a refrigerator. Recrystallization of the solid from petroleum ether afforded 2.8 g (44%) of colourless crystals.

2-(4-Methoxyphenyl)-2-(4-fluorophenyl)propane

To a suspension of 6.7 g (50 mmol) of AlCl_3 in 18 ml of anisole was added dropwise with stirring and cooling to 10° a solution consisting of 9.2 g (60 mmol) of 2-(4-fluorophenyl)propan-2-ol in 18 ml of anisole. The reaction mixture was left overnight and then decomposed with ice and dilute hydrochloric acid. The organic layer was separated, washed with water, dried over Na_2SO_4 and the solvent removed. The residue was distilled *in vacuo* giving 10.7 g (73%) of a colourless oil.

2-(4-Fluorophenyl)-2-(3,4,5-Trichlorophenyl)propane

To a suspension of 1.1 g (8 mmol) of AlCl_3 in 5 ml of fluorobenzene was added with stirring and cooling to 10° a solution consisting of 2.15 g (9 mmol) of 2-(3,4,5-trichlorophenyl)propan-2-ol in 15 ml of fluorobenzene. The reaction mixture was left overnight and then decomposed with ice and dilute hydrochloric acid. The organic layer was separated, washed with water, dried over Na_2SO_4 and the solvent removed. The residue was distilled under reduced pressure and recrystallized from petroleum ether, yielding colourless crystals.

(3-Fluorophenyl)phenyl sulphide

A solution of 5.55 g (50 mmol) of 3-fluoroaniline in a mixture of 13.5 ml of concentrated hydrochloric acid and 25 ml of water was diazotized at $0\text{--}5^\circ$ by addition

of 3.7 g of NaNO_2 in 15 ml of water. The diazo solution formed was added dropwise to a solution of 5.5 g (50 mmol) of thiophenol and 8.3 g of NaOH in 75 ml of water heated to 60° . After stirring for 1 h on a steam bath, the reaction mixture was steam-distilled. The distillate was extracted with petroleum ether, washed with a dilute solution of NaOH and water, and then dried over Na_2SO_4 . After evaporation of the solvent, the residue was distilled *in vacuo* giving 2.7 g (26%) of a pale yellow oil with b.p. $118^\circ/2$ mmHg. (Found: C, 70.00; H, 4.44. $\text{C}_{12}\text{H}_9\text{FS}$ calcd.: C, 70.55; H, 4.45%.)

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