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STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

XX *. STRUCTURE AND SPECTROSCOPIC PROPERTIES OF TRIPHENYLIODOMETHYLTIN(IV)

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Summary

The structure of the title compound has been determined from X-ray diffractometer intensity data using Patterson and Fourier techniques. Crystals are triclinic, space group $P\bar{1}$, with a 7.3626(5), b 10.7516(2), c 13.2404(3) Å, α 106.12(4), β 94.81(6), γ 114.26(6)°, and are composed of discrete non-interacting Ph_3SnCH_2I molecules. The geometry at tin is only slightly distorted from ideal tetrahedral, with C—Sn—C bond angles lying in the range 106.3(2) to 111.8(2)°. The mean Sn—C(Ph) bond distance (2.133(6) Å) is exactly the same as the $Sn—CH_2I$ distance (2.134(6) Å). Thus the presence of the bulky, electronegative iodine substituent on the alkyl group has a negligible effect on the stereochemistry at tin. This observation is consistent with the narrow single line seen in the Mössbauer spectrum, but the ^1H and ^{119}Sn NMR data show that some perturbation of the electronic distribution occurs. Mass spectral data are also reported.

Introduction

To date, structural investigations of tetraorganostannanes have been very largely restricted to studies of tetraphenyltin [2,3], its 3- or 4-phenyl-substituted analogues [4—7], and carbocyclic derivatives such as tetracyclopentadienyltin [8] and triphenyl-7-cyclohepta-1,3,5-trienyltin [9]. The structures of only two halo-substituted tetraorganostannanes, $Me_2PhSn(CPh{=}CPhCPh{=}CPhX)$ (X = Cl, Br), have been reported [10], and both possess four-coordinate geometries with no intramolecular tin—halogen interaction, although a weak interac-

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* For part XIX see ref. 1.

tion may be induced when the phenyl group is replaced by a bromine [11]. In halomethyltin compounds the halogen atom is necessarily situated very close to the tin atom, and is therefore best placed to influence the geometry and bonding at the metal. In order to study the effect of α-halo-substitution, we have determined the structure of triphenyliodomethyltin and also investigated its spectroscopic properties.

Experimental

Crystal preparation. Triphenyliodomethyltin was prepared by the method of Seyferth and Andrews [12] (Found: C, 46.35; H, 3.81. $C_{19}H_{17}SnI$ calcd.: C, 46.48; H, 3.49%). Translucent, prismatic crystals, stable to air and X-rays, were obtained by recrystallisation from n-hexane, and a crystal of approximate dimensions 0.5 × 0.5 × 0.2 mm mounted on a glass fibre used to collect cell and intensity data.

Crystal data. $C_{19}H_{17}ISn$, M 490.94, Triclinic, a 7.3626(5), b 10.7516(2), c 13.2404(3) Å, α 106.12(4), β 94.81(6), γ 114.26(6)°, U 914.66 Å^3, $Z = 2$, $F(000) = 468$, D_m 1.80 g cm^{-3} (flotation), D_c 1.79 g cm^{-3}, Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 31.02 cm^{-2}, Space group $P\overline{1}$.

Cell measurements and data collection. Initial cell parameters and space group determination were elucidated from oscillation and zero- and first-layer Weissenberg photographs. The intensities of 5160 reflections were measured by use of a Hilger and Watts four-circle automatic diffractometer. Reflections with intensities $I < 3\sigma(I)$ were considered non-observed, reducing the number of usable reflections to 4618. Accurate unit cell dimensions were obtained by least-squares refinement of ca. 20 reflections. Lorentz and polarisation corrections were applied, but none were made for absorption effects due to the low μ value.

Structure determination and refinement. The positional parameters of the tin and iodine atoms in the asymmetric unit were deduced from a three-dimensional Patterson synthesis, and used to phase the initial structure factor calculation. A Fourier synthesis at this stage revealed no light atoms which would fit a chemically acceptable model, thus the positional parameters of the two heavy atoms were refined by four cycles of full matrix isotropic least-squares refinement. A subsequent Fourier synthesis yielded the positions of all the non-hydrogen light atoms. One cycle of full-matrix isotropic least-squares refinement, followed by four cycles of full-matrix anisotropic least-squares refinement, produced convergence of the "R"-value at 0.0634. By inspection of the values of $\Delta(F_o - F_c)^2$, the weighting scheme $w = 1/(1 + [(F_o - P_2)/P_1]^2)$ where $P_1 = 21.0$, $P_2 = 14.0$ was introduced. The calculated positions of sixteen hydrogen atoms were also included, although neither their positional nor thermal parameters were further refined. Four subsequent cycles of full-matrix anisotropic least-squares refinement produced a final "R"-value of 0.0628.

Final atomic coordinates and anisotropic thermal parameters of all non-hydrogen light atoms are listed in Tables 1 and 2, respectively. The calculated atomic coordinates of the hydrogen atoms are given in Table 3. Intramolecular bond distances and angles are listed in Table 4. The atomic labelling is shown in Fig. 1.

Scattering factors used were those for neutral atoms [13], and the refinement was carried out using the CRYSTALS suite of programmes [14].

TABLE 1

FINAL FRACTIONAL ATOMIC COORDINATES (with estimated standard deviations in parentheses)

Atom	x/a	y/b	z/c
Sn(1)	0.21770(5)	0.04519(4)	0.22451(3)
C(1)	0.1212(9)	0.1936(6)	0.1877(5)
C(2)	0.2280(10)	0.2791(7)	0.1302(6)
C(3)	0.1780(10)	0.3834(8)	0.1130(7)
C(4)	0.0210(10)	0.4020(9)	0.1509(8)
C(5)	−0.0880(10)	0.3200(10)	0.2066(8)
C(6)	−0.0370(10)	0.2142(8)	0.2256(6)
C(7)	0.4717(8)	0.1717(6)	0.3600(5)
C(8)	0.5650(10)	0.1089(8)	0.4093(6)
C(9)	0.7280(10)	0.1950(10)	0.4992(7)
C(10)	0.8020(10)	0.337(10)	0.5406(7)
C(11)	0.7060(10)	0.4030(10)	0.4950(8)
C(12)	0.5400(10)	0.3191(8)	0.4035(7)
C(13)	−0.0201(8)	−0.1201(6)	0.2602(5)
C(14)	−0.0920(10)	−0.0871(8)	0.3512(5)
C(15)	−0.2570(10)	−0.1940(10)	0.3740(6)
C(16)	−0.3410(10)	−0.3359(9)	0.3038(8)
C(17)	−0.2691(10)	−0.3707(8)	0.2148(8)
C(18)	−0.1100(10)	−0.2648(7)	0.1919(7)
C(19)	0.3090(10)	−0.0501(8)	0.0870(5)
I(1)	0.43712(9)	−0.18699(6)	0.11361(5)

Spectroscopic measurements. ^1H NMR measurements were recorded using a Varian HA-100 instrument. ^{119}Sn chemical shifts were obtained by the INDOR method using the same instrument equipped with a Schlumberger frequency syn-

TABLE 2

FINAL ANISOTROPIC THERMAL PARAMETERS (with estimated standard deviations in parentheses) [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	3.69(2)	4.18(2)	4.91(2)	1.96(2)	1.28(1)	1.81(1)
C(1)	4.4(3)	4.7(3)	5.0(3)	1.9(2)	1.1(2)	2.4(2)
C(2)	4.7(3)	5.4(3)	7.0(4)	3.1(3)	1.8(3)	2.2(3)
C(3)	7.1(4)	5.2(3)	7.8(5)	3.3(3)	1.4(4)	2.5(3)
C(4)	7.5(5)	5.7(4)	9.0(5)	2.8(4)	0.3(4)	4.0(4)
C(5)	6.7(4)	7.6(5)	8.5(5)	2.3(4)	2.2(3)	5.2(4)
C(6)	5.3(3)	7.0(4)	5.7(3)	2.3(3)	1.7(3)	3.6(3)
C(7)	3.7(2)	4.3(3)	5.5(3)	1.8(2)	1.2(2)	1.5(2)
C(8)	5.3(3)	6.6(4)	5.8(3)	2.3(3)	1.0(3)	2.9(3)
C(9)	6.5(4)	10.4(7)	5.9(4)	2.1(4)	0.1(3)	0.5(5)
C(10)	5.5(4)	9.7(7)	6.3(5)	−0.1(5)	0.1(3)	1.1(4)
C(11)	6.6(5)	6.2(4)	8.0(5)	−0.1(4)	0.3(4)	0.9(4)
C(12)	5.8(4)	4.7(3)	7.4(4)	1.7(3)	1.4(3)	1.6(3)
C(13)	3.7(2)	4.2(2)	5.2(3)	2.2(2)	0.9(2)	1.6(2)
C(14)	5.0(3)	5.9(3)	5.3(3)	2.5(3)	1.2(3)	1.8(3)
C(15)	5.0(3)	8.7(5)	6.7(4)	4.2(4)	2.3(3)	2.7(3)
C(16)	4.9(3)	6.5(4)	11.7(7)	5.7(5)	3.3(4)	1.9(3)
C(17)	5.6(4)	4.7(3)	11.2(7)	2.8(4)	2.9(4)	2.3(3)
C(18)	5.0(3)	4.7(3)	8.1(5)	1.5(3)	2.5(3)	1.9(3)
C(19)	7.1(4)	5.9(3)	5.1(3)	2.3(3)	2.5(3)	3.7(3)
I(1)	7.24(3)	7.79(4)	7.86(4)	2.56(3)	1.74(3)	4.87(3)

[a] U_{ij} are of the form $10^2 \exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2klU_{23}b^*c^* + 2hlU_{13}a^*c^*)]$.

TABLE 3

CALCULATED FRACTIONAL ATOMIC COORDINATES FOR HYDROGEN ATOMS[a]

Atom	*x/a*	*y/b*	*z/c*
H(1)	0.3431	0.2629	0.0988
H(2)	0.2568	0.4445	0.0687
H(3)	−0.0112	0.4806	0.1391
H(4)	−0.2043	0.3358	0.2357
H(5)	−0.1191	0.1509	0.2670
H(6)	0.5167	−0.0002	0.3773
H(7)	0.7958	0.1480	0.5355
H(8)	0.9132	0.4088	0.6055
H(9)	0.7551	0.5146	0.5259
H(10)	0.4741	0.3681	0.3687
H(11)	−0.0605	−0.2880	0.1218
H(12)	−0.3321	−0.4767	0.1643
H(13)	−0.4604	−0.4124	0.3209
H(14)	−0.3114	−0.1683	0.4405
H(15)	−0.0269	0.0157	0.4031
H(16)	0.4154	0.0321	0.0671
H(17)	0.1880	−0.1064	0.0233

[a] All hydrogen atoms were assigned an isotropic thermal parameter of 0.05.

TABLE 4

INTRAMOLECULAR BOND DISTANCES (Å) AND ANGLES (°) (with estimated standard deviations in parentheses).

(a) Bond distances			
Sn(1)—C(1)	2.143(6)	C(7)—C(8)	1.38(1)
Sn(1)—C(7)	2.135(6)	C(8)—C(9)	1.39(1)
Sn(1)—C(13)	2.120(5)	C(9)—C(10)	1.32(2)
Sn(1)—C(19)	2.134(6)	C(10)—C(11)	1.39(2)
C(1)—C(2)	1.39(1)	C(11)—C(12)	1.42(1)
		C(12)—C(7)	1.37(1)
C(2)—C(3)	1.39(1)		
C(3)—C(4)	1.36(1)	C(13)—C(14)	1.37(1)
C(4)—C(5)	1.36(1)	C(14)—C(15)	1.41(1)
C(5)—C(6)	1.42(1)	C(15)—C(16)	1.38(1)
C(6)—C(1)	1.38(1)	C(16)—C(17)	1.35(1)
C(19)—I(1)	2.134(7)	C(17)—C(18)	1.39(1)
		C(18)—C(13)	1.40(1)
(b) Bond angles			
C(1)—Sn(1)—C(7)	106.3(2)	Sn(1)—C(1)—C(2)	119.6(4)
C(1)—Sn(1)—C(13)	111.8(2)	Sn(1)—C(1)—C(6)	121.7(5)
C(1)—Sn(1)—C(19)	107.5(3)	C(2)—C(1)—C(6)	118.6(6)
C(7)—Sn(1)—C(13)	110.7(2)	C(1)—C(2)—C(3)	120.2(7)
C(7)—Sn(1)—C(19)	110.7(3)	C(2)—C(3)—C(4)	120.4(7)
C(13)—Sn(1)—C(19)	109.7(3)	C(3)—C(4)—C(5)	121.3(7)
Sn(1)—C(19)—I(1)	113.1(3)	C(4)—C(5)—C(6)	119.0(7)
		C(5)—C(6)—C(1)	120.6(7)
Sn(1)—C(7)—C(8)	121.9(5)	Sn(1)—C(13)—C(14)	120.6(4)
Sn(1)—C(7)—C(12)	119.8(5)	Sn(1)—C(13)—C(18)	121.4(5)
C(8)—C(7)—C(12)	118.2(6)	C(14)—C(13)—C(18)	118.0(6)
C(7)—C(8)—C(9)	120.2(7)	C(13)—C(14)—C(15)	121.7(7)
C(8)—C(9)—C(10)	123.2(9)	C(14)—C(15)—C(16)	118.0(7)
C(9)—C(10)—C(11)	117.8(8)	C(15)—C(16)—C(17)	121.0(6)
C(10)—C(11)—C(12)	120.7(8)	C(16)—C(17)—C(18)	120.6(7)
C(11)—C(12)—C(7)	119.8(7)	C(17)—C(18)—C(19)	120.7(7)

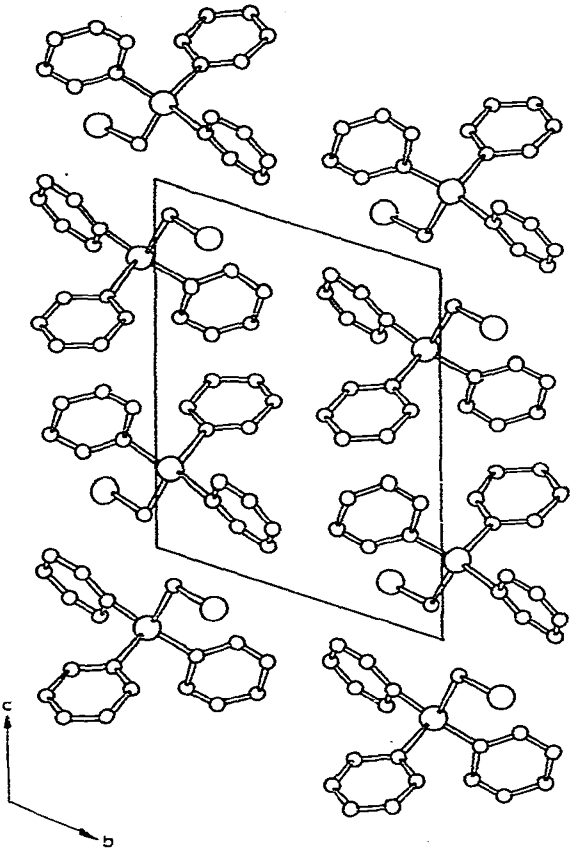

Fig. 1. Projection of the unit cell of Ph_3SnCH_2I onto the bc plane.

thesiser and synthesiser driver, and chemical shifts are quoted relative to Me_4Sn = 0. All data were obtained in benzene solution (ca. 20% w/v). A sample of triphenylchloromethyltin was obtained from treating the iodomethyltin compound with silver chloride in acetonitrile for seven days [12].

Tin-119*m* Mössbauer data were recorded using Harwell instrumentation as before [1] against a $BaSnO_3$ source (5 mci, The Radiochemical Centre, Amersham). Isomer shifts are quoted with respect to SnO_2 = 0, and are accurate to better than ± 0.05 mm s^{-1}. Quadrupole splittings are accurate to better than ± 0.10 mm s^{-1}. Data reduction and refinement was carried out by usual least-squares fitting methods.

Mass spectra were obtained at 70 eV using an AEI MS-902 instrument.

Discussion

Crystals of triphenyliodomethyltin(IV) consist of discrete monomeric molecular units with no intermolecular interaction (Fig. 2). The geometry at the tin atom is almost regular tetrahedral (Fig. 1), with angles at tin lying in the range 106.3(2) to 111.8(2)° compared with a value of 109.8° expected for regular tetrahedral geometry. In Table 5 are compared Sn—C(Ph) and Sn—C(alkyl) bond

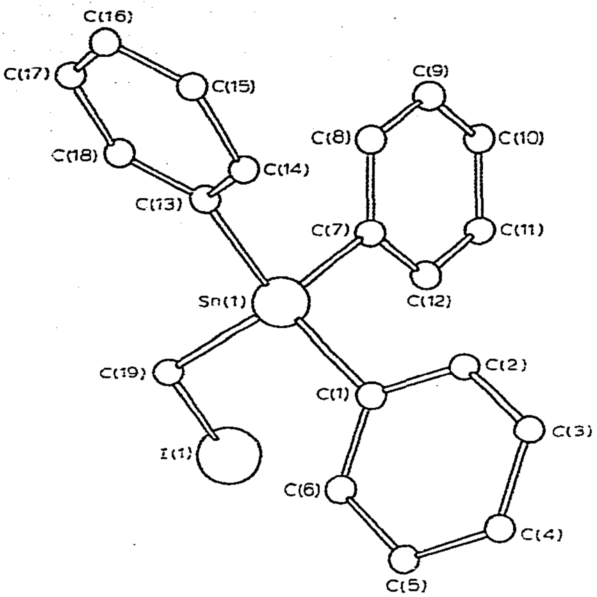

Fig. 2. The structure of Ph_3SnCH_2I showing atomic numbering.

distances in Ph_3SnCH_2I and related molecules, from which it can be seen that those for Ph_3SnCH_2I fall within the same range as previously observed. The Sn···I intraatomic distance of 3.55 Å is greater than the covalent Sn—I bond distance previously reported for $Ph_2ISn(CH_2)_4SnIPh_2$ [15] (2.729 Å), and also in excess of the sum of the expected covalent radii (2.73 Å). The distance is, however, shorter than the sum of the respective Van der Waals' radii (4.33 Å), although according to Pauling [16] this estimate is ca. 0.5 Å too large for for an interaction close to a covalent bond direction, as in this case. Thus, although on this basis some interaction between the iodine and tin atoms might be expected, none may be discerned from distortions of the bond angles at tin.

The mass spectrum of Ph_3SnCH_2I, recorded at an ionisation chamber temperature of 90°C, contains no fragments of *m/e* value greater than that of the parent ion. An inspection of the fragmentation processes (Fig. 3) confirms the influence

TABLE 5

COMPARISON OF TIN—LIGAND BOND DISTANCES IN Ph_3SnCH_2I WITH THOSE IN RELATED COMPOUNDS (Å)

Compound[a]	*r*(Sn—C(Ph))	*r*(Sn—C(alkyl))	*r*(Sn—I)	Reference
Ph_3SnCH_2I	2.133(6)[b]	2.134(6)	3.55(1)	This work
Ph_4Sn	2.14(2)			27
Ph_3SnCl	2.12(2)			29
Ph_2SnCl_2	2.11(4)[b]			30
$(PhCH_2)_4Sn$		2.18(1)[b]		31
$Ph_2ISn(CH_2)_4SnIPh_2$	2.15(2)[b]	2.14(2)	2.729(3)	15

[a] All examples have either regular or distorted tetrahedral geometries. [b] Mean value.

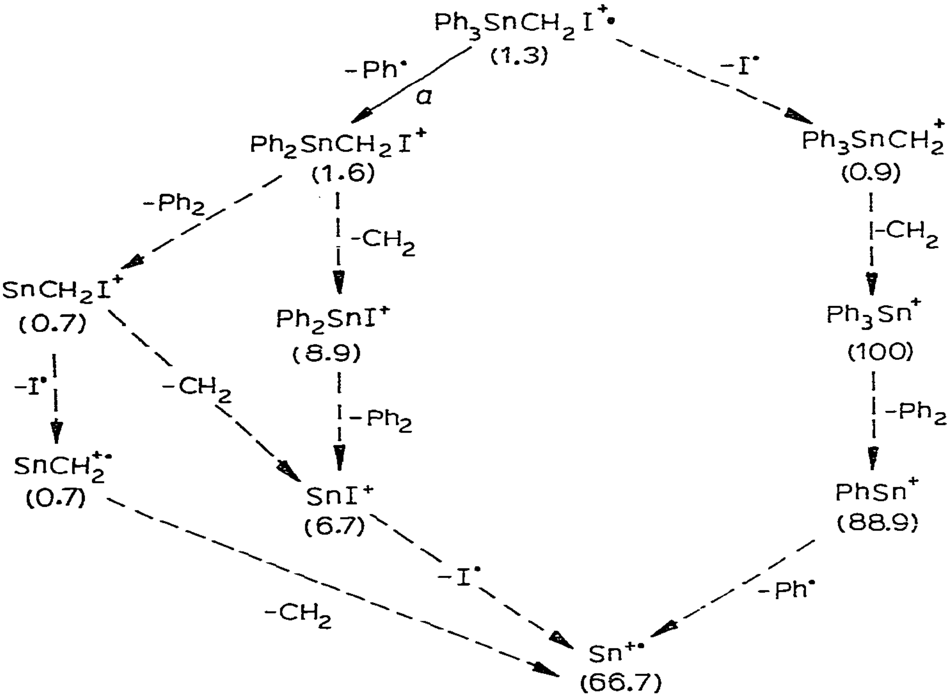

Fig. 3. Fragmentation pattern for Ph_3SnCH_2I. The solid line represents a pathway confirmed by the observation of metastable ions. Abundances relative to the most intense tin-containing fragment are shown in parentheses. [a] $m^{\star}_{calc} = 346$—350; $m^{\star}_{obs} = 346$—351.

of odd bonding- or even bonding-electron character of an ion on its dissociation reactions as outlined by McLafferty [17]. Previous observations [18] indicate even-electron ions, particularly ones in which tin has an odd coordination number, to be the major carriers of the ion current. Thus, in the mass spectrum of Ph_3SnCH_2I, Ph_3Sn^+, Ph_2SnI^+ and $PhSn^+$ are the most abundant fragments observed. The relatively high abundance of the $Sn^{+\cdot}$ ion reflects the relatively weak nature of the tin—phenyl and tin—methylene bonds.

In the fragmentation processes, it can be seen that even-electron ions tend to lose even-electron neutral fragments, viz.:

$Ph_3Sn^+ \rightarrow PhSn^+ + Ph_2$

$Ph_2SnI^+ \rightarrow SnI^+ + Ph_2$

odd-electron ions, such as the parent $P^{+\cdot}$ ion fragment via bond cleavage to yield an odd-electron radical and an even-electron ion, viz.:

$Ph_3SnCH_2I^{+\cdot} \rightarrow Ph_2SnCH_2I^+ + Ph^\cdot$

The principal fragmentation processes occurring in the mass spectrum of Ph_3SnCH_2I are (a) loss of $Ph^\cdot$, either as a radical or as biphenyl, and (b) the elimination of methylene e.g.:

$Ph_2SnCH_2^+ \rightarrow Ph_3Sn^+ + CH_2$

$Ph_nSnCH_2I^+ \rightarrow Ph_nSnI^+ + CH_2 \qquad n = 0, 2$

the latter process involving an intramolecular 1,2-shift of the iodine atom.

The tin-119*m* Mössbauer data for Ph_3SnCH_2I and related compounds are listed in Table 6. None of the compounds listed exhibits a quadrupole splitting, indicating a cubic electric field at the tin nucleus and negligible distortion from tetrahedral geometry for any of the compounds. In the present case, the narrow linewidth observed for Ph_3SnCH_2I ($\Gamma = 0.96$ mm s^{-1}) precludes the presence of an unresolved splitting. The isomer shifts of all the examples listed fall into a quite narrow range (1.23—1.30 mm s^{-1}), irrespective of the substituent on the alkyl chain. Indicating that the total tin 5*s* electron density is the same (within experimental error) for every compound. This constancy of the isomer shift may be rationalised in terms of two complementary effects [19]. The increased electronegativity of the iodomethyl group (over for example the methyl group) will increase the positive charge on the tin, which will cause a contraction of the tin 5*s* orbital, thereby compensating for the loss of electron density to the electronegative ligand by virtus of the —I effect of the latter.

The replacement of an organic group in a tetraorganostannane by a more electronegative group would be expected to cause rehybridisation at the tin, in which the *s*-character of the Sn—C bonds and the *p*-character of the Sn—ligand bond are both increased [20]. In Ph_3SnCH_2I, the crystallographic data confirms the expectation of the Mössbauer results, that deviations from regular tetrahedral geometry will be small. The mean values of both the C_{alkyl}—Sn—Cl(Ph) and C(Ph)—Sn—C(Ph), 109.3 and 109.6°, respectively, are very close to the tetrahedral value, whilst the Sn—C(alkyl) bond distance shows no increase over the mean Sn—C(Ph) distance. Thus the extent of rehybridisation is very small.

Table 7 lists ^1H and ^{119}Sn magnetic resonance data for Ph_3SnCH_2I and related compounds. The substitution of a more electronegative group, i.e. I or Cl, for a methyl proton causes a downfield shift of the ^1H resonance, the magnitude of the shift being reflected by the nature of the substituent: $H < I < Cl$. This can be directly correlated with a deshielding of the proton nucleus by the inductive effect of the electronegative group [21].

The two-bond coupling constant $^2J(^{119}Sn—C—^1H)$ can be used as a guide to the *s*-electron character of a tin—carbon bond. However, the decrease in *s*-character of the $Sn—CH_2I$ bond caused by small rehybridisation changes [20] will not explain the drastic decrease in tin—proton coupling constants observed for Ph_3SnCH_2I and Ph_3SnCH_2Cl. Verdonck and coworkers [21] have suggested the empirical relationship:

$$^2J(\mathrm{Sn{-}C{-}H}) \simeq \Phi^2_{\mathrm{Sn}}(0) \cdot \Phi^2_{\mathrm{H}}(0) \cdot \frac{1}{\lambda(\mathrm{Sn{-}C})}$$

as a guide to tin—proton coupling constants in compounds $(XCH_2)_nSnX_{4-n}$, where $\Phi_{Sn}(0)$ and $\Phi_H(0)$ are the electron densities around the tin and the coupling proton respectively, and $\lambda(Sn—C)$ the polarity of the Sn—C bond. Since $\Phi_{Sn}(0)$ has been seen to remain largely unaffected by the presence of a more electronegative CH_2X group (Mössbauer isomer shift data), the decrease in tin—proton coupling constants is due partly to the small increase in $\lambda(Sn—C)$, but mainly due to the decrease in the electron density at the coupled proton (reflected in the ^1H chemical shifts) in the presence of the electron-withdrawing group. This rationalisation also accounts for the magnitude of the decrease in

TABLE 6

TIN-119*m* MÖSSBAUER DATA FOR Ph_3SnCH_2I AND RELATED COMPOUNDS (mm s^{-1}).

Compound	*IS*	*QS*	Reference
Ph_3SnCH_2I	1.25	0	This work
Ph_3SnCH_3	1.23	0	24
$Ph_3SnCH_2CH_2CF_3$	1.23	0	25
$Ph_3Sn(CH_2)_6CH_3$	1.27	0	26
$Ph_3SnCH_2CH{=}CH_2$	1.30	0	27

coupling constant with respect to the electronegativity of the substituent present.

Although the Mössbauer isomer shifts are constant within experimental error, the ^{119}Sn NMR chemical shifts for Ph_3SnCH_2I and Ph_3SnCH_2Cl exhibit large upfield shifts from that of Ph_3SnCH_3. On simple electronegativity grounds, the presence of increasingly electronegative groups should produce increasing shifts to low field of Me_4Sn. This, however, is observed neither in the case of Ph_3SnCH_2I and Ph_3SnCH_2Cl nor in the case of the organotin halides, R_nSnX_{4-n}, where initial replacement by a halogen of an organic group produces the expected shift to low field, but for $n = 3, 4$, this trend is reversed, and shifts to high field are observed [22].

In the case of Ph_3SnCH_2I and Ph_3SnCH_2Cl, two factors can explain the increased shielding at tin, and hence the resonance shift to high field to Me_4Sn. Firstly, since the paramagnetic contribution is considered to dominate the shielding, this will reach a maximum when the degree of inbalance in the bonds to tin is greatest [22]. Rehybridisation in the tin-carbon bond framework in the presence of the $-CH_2I$ group has been shown to be small, but appears to be large enough to contribute to the chemical shifts. Secondly, the polarisability of the adjacent iodine atom can lead to high field shifts [22,23], and this may also contribute to the observed shifts. In the case Ph_3SnCH_2Cl, only an imbalance in the σ-framework resulting from rehybridisation can account for the observed chemical shift, and therefore it must be concluded that the extent of the bonding orbital imbalance is far greater here than in the iodo derivative.

TABLE 7

^1H AND ^{119}Sn NMR DATA FOR Ph_3SnCH_2I AND RELATED R_3SnCH_2X COMPOUNDS

R	X	$\tau(^1H)$ (ppm)	$^2J(^{119,117}Sn{-}C{-}H)$ (Hz)	$\tau(^{119}Sn)^a$ (ppm)	Reference
Ph [b]	I	7.63	23.4, 20.2	—121.7 ± 1	This work
Ph	I	7.67	22.0 [c]		12
Ph [d]	Cl	6.48	21.4, 17.8	—133.2 ± 1	This work
Ph	H	9.28 [e]	57.0 [c,e]	—93	32
				—98	33
Ph	CH_3			—111.1	34
				—113.7	35
Cl	Cl	5.92	19.4 [c]		36

[a] Negative shifts are to high field of Me_4Sn (= 0). [b] $\tau(^1H)$ for phenyl protons: 2.70—2.80 ppm. [c] Unresolved. [d] $\tau(^1H)$ for phenyl protons: 2.36—2.60 ppm. [e] Ref. 37.

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