Magnetic Double Resonance Studies of Tin-119 Chemical Shifts in Compounds with Tin–Sulphur Bonds and Related Species

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Tin-119 chemical shifts and selected other n.m.r. parameters are reported for 103 compounds, many of which are hitherto unreported species. The effect of changing a group at a site remote from the tin atom depends upon the substituents on tin and this is attributed to the mobility of the electrons in groups such as phenyl and to a degree of π-interaction with the tin atom. In series SnX_nY_{4-n} the departure from linearity of plots of $\delta(^{119}Sn)$ against n depends partly upon the electronegativity difference between X and Y, but also upon other factors. A method of obtaining a quantitative estimate of this deviation is presented.

THE following factors have been suggested [1] as having significant effects upon the magnetic shielding of ^{119}Sn: (a) electronegativity of substituents; [2] (b) multiple bonding, specifically $d\pi \longleftarrow p\pi$; [3,4] (c) diamagnetic circulation of electrons in substituents; [5] (d) electronic excitation energies; [6] (e) interbond angles; [1,7] (f) Polarizability of substituents.[8] Evidence in support of (a), (d), and (e) is available, but the complex interplay of (b), (c), and (f) makes it difficult to discriminate among them and each has individually been proposed to account for observed shifts of the ^{119}Sn resonance to high field when the tin atom is bound to one or more bulky atoms. Calculations of the magnitude of (c) show that it alone is too small to account for all of the observed high field shifts and that therefore presumably (b) and/or (f) are also involved.[9]

In this paper we report measurements aimed at clari-

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fying the importance of (a)—(c) and (f) in 103 closely related organotin compounds, most of which have at least one tin–sulphur bond. Tin-119 chemical shifts appear to be especially sensitive to small changes in the tin–sulphur bond (brought about, for example, by a change from *S*-methyl to *S*-ethyl) and thus in principle should be a delicate probe into the extent of any $d\pi$–$p\pi$ bonding between tin and sulphur.

The tin-119 chemical shifts were obtained by the ^1H-{^{119}Sn} double resonance technique[4] because this offers considerable advantages in terms of convenience, sensitivity, and the ability to relate unequivocally resonances in the ^1H and the ^{119}Sn spectra.

EXPERIMENTAL

The compounds $4\text{-}XC_6H_4SSnPh_3$, $(4\text{-}XC_6H_4S)_2SnMe_2$, $4\text{-}XC_6H_4SSnMe_3$, and $Ph_{4-n}Sn(SR)_n$ were made by reaction between $Me_{4-n}SnCl_n$ or $Ph_{4-n}SnCl_n$ and the appropriate thiol in the presence of base (usually Et_3N) and were generally purified by distillation or recrystallisation from light petroleum. Analytical data and m. or b.p.s. for previously unreported compounds are in Table 1. The compounds $4\text{-}XC_6H_4SCH_2SnPh_3$ were prepared from Ph_3SnCH_2I and a thiol $4\text{-}XC_6H_4SH$ in the presence of base.[10] Species SnX_nY_{4-n} (X,Y = RS, RSe, halogen, *etc.*) were made by mixing weighed amounts of SnX_4 and SnY_4 with solvent in an n.m.r. tube and assignments of lines in the ^1H spectra were confirmed by varying the proportions of the components. Equilibration was generally complete within a few minutes and no attempts were made to isolate intermediate species.

TABLE 1

Analytical data for new compounds

No.	Compound	B.p. (°C) [*p*/mmHg] M.p./°C	Found (%)			Calc. (%)		
			C	H	S or Se	C	H	S or Se
(3)	$Ph_2Sn(SMe)_2$	146—150 [0.2]	45.8	4.4	17.25	45.8	4.4	17.45
(4)	$PhSn(SMe)_3$	146 [0.4]	32.3	4.2	28.6	32.1	4.2	28.5
(6)	Ph_3SnSEt	67—68	58.6	4.8	7.85	58.4	4.9	7.8
(7)	$Ph_2Sn(SEt)_2$	176 [0.25]	48.8	5.05	16.1	48.6	5.1	16.2
(8)	$PhSn(SEt)_3$	156 [0.4]	38.9	5.35	24.9	38.0	5.3	25.4
(10)	Ph_3SnSPr^i	68—70	58.7	4.9	6.85	59.3	5.2	7.55
(11)	$Ph_2Sn(SPr^i)_2$	166 [0.2]	51.1	5.7	15.1	51.1	5.7	15.2
(12)	$PhSn(SPr^i)_3$	155 [0.5]	43.0	6.25	22.7	42.8	6.2	22.8
(14)	Ph_3SnSBu^t	124—126	60.1	5.35	7.45	60.0	5.5	7.3
(15)	$Ph_2Sn(SBu^t)_2$	186 [0.1] [a]	53.5	6.25	14.1	53.2	6.25	14.2
(16)	$PhSn(SBu^t)_3$	155—158 [0.2]	46.7	6.85	20.6	46.7	6.95	20.8
(20)	$PhSn(SBz)_3$	Decomp. 230 [0.06] [b]	57.2	4.45	16.9	57.4	4.65	17.0
(23)	$Ph_2Sn(SeMe)_2$	*ca.* 180 [0.04]	36.5	3.5	34.55	36.5	3.5	34.25
(26)	$Me_3SnSCPh_3$	65—66.5	60.2	5.35	7.35	60.2	5.5	7.3

[a] Crystallised on standing. [b] Purified by solvent extraction.

^1H N.m.r. spectra were recorded at 23° on a spectrometer operating at a measuring frequency of 60 MHz and ^1H-{^{119}Sn} and ^1H-{^{77}Se} double resonance experiments were performed as described elsewhere.[4] $\Xi(^{119}Sn)$ for Me_4Sn is taken to be 37 290 665 Hz.

RESULTS

Table 2 lists the ^{119}Sn chemical shifts in the isolable compounds studied in this work. These were obtained by observing the ^{119}Sn satellites of the *Sn*-methyl proton resonances wherever possible [$^2J(^{119}Sn\text{–}H)$ *ca.* 60 Hz] or of the Ph *o*-proton resonances [$^3J(^{119}Sn\text{–}H)$ *ca.* 40 Hz] in other cases. The value for Ph_4Sn was obtained in 1,1,2-trichloroethane solution at 104° because this compound has very low solubility in normal n.m.r. solvents at room temperature. The result is *ca.* 10 p.p.m. to higher field than that previously estimated by extrapolation from series of related molecules. No significant concentration dependence of $\delta(^{119}Sn)$ was observed except in the case of *p*-amino-derivatives which presumably can associate weakly through the formation of N ⟶ Sn links. In the mixtures (n.m.r. data in Table 3) separate resonances were detected for the various species, indicating that the life-times were long on an n.m.r. time-scale, *i.e.* in excess of 0.1 s. However, it was generally observed that the line widths varied for the different species present in any particular mixture indicating a range of life-times. Qualitatively it was found that the life-times associated with different substituents decreased in the orders $I > Br > Cl$ for halogens and $Bu^tSe \geq Bu^tS \gg PhSe, PhS > MeSe \geq MeS, SCH_2Ph$ for chalcogenides. Detailed studies of the equilibrium constants in these systems have not been undertaken but they appear to be close to unity since the relative intensities of the signals from the various species were close to those expected on a simple statistical basis, although tendencies to favour the intermediate species were noted. We have been unable to identify three of the species present in certain of these mixtures; however, their n.m.r. parameters are included in Table 3.

DISCUSSION

The results for the benzenethiolates [(27)—(34) and (42)—(48)] show a small but real dependence upon the nature of the *para*-substituent. The direction of this effect confirms previous observations[2] that electron-withdrawing substituents decrease the tin shielding, an increase in the Hammett constant σ_{para} for X of one unit giving algebraic increases of *ca.* 15, 4, and 6 p.p.m. respectively in the series $4\text{-}XC_6H_4SSNMe_3$, $4\text{-}XC_6H_4SSnPh_3$, and

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[10] R. A. Taylor and J. L. Wardell, *J. Organometallic Chem.*, in the press.

TABLE 2

^{119}Sn Chemical shifts in isolable organotin species

No.	Compound	$\delta(^{119}Sn)$/p.p.m.[a]	Notes
(1)	Ph_4Sn	-137 ± 2	$CHCl_2CH_2Cl$ soln at 110°
(2)	Ph_3SnSMe	-47 ± 1	*ca.* 30% soln. in CH_2Cl_2
(3)	$Ph_3Sn(SMe)_2$	$+38.5 \pm 1$	*ca.* 30% soln. in CH_2Cl_2
(4)	$PhSn(SMe)_3$	$+107 \pm 2$	*ca.* 30% soln. in CH_2Cl_2
(5)	$Sn(SMe)_4$	$+165 \pm 1$	Neat
(6)	Ph_3SnSEt	-54.4 ± 2	*ca.* 30% soln. in CH_2Cl_2
(7)	$Ph_2Sn(SEt)_2$	$+33 \pm 2$	*ca.* 30% soln. in CH_2Cl_2
(8)	$PhSn(SEt)_3$	$+90 \pm 2$	*ca.* 30% soln. in CH_2Cl_2
(9)	$Sn(SEt)_4$	$+138$	Neat
(10)	Ph_3SnSPr^i	-62 ± 1	*ca.* 30% soln. in CH_2Cl_2
(11)	$Ph_2Sn(SPr^i)_2$	$+9.5 \pm 2$	*ca.* 30% soln. in CH_2Cl_2
(12)	$PhSn(SPr^i)_3$	$+69.5 \pm 2$	*ca.* 30% soln. in CH_2Cl_2
(13)	$Sn(SPr^i)_4$	$+106.5 \pm 1$	Neat
(14)	Ph_3SnSBu^t	-84.2 ± 1	*ca.* 30% soln. in CH_2Cl_2
(15)	$Ph_2Sn(SBu^t)_2$	-30.4 ± 2	*ca.* 30% soln. in CH_2Cl_2
(16)	$PhSn(SBu^t)_3$	$+11 \pm 2$	*ca.* 30% soln. in CH_2Cl_2
(17)	$Sn(SBu^t)_4$	$+26 \pm 1$	Neat
(18)	Ph_3SnSBz	-54.5 ± 2	*ca.* 30% soln. in CH_2Cl_2
(19)	$Ph_2Sn(SBz)_2$	$+26 \pm 2$	*ca.* 30% soln. in CH_2Cl_2
(20)	$PhSn(SBz)_3$	$+87.5 \pm 2$	*ca.* 30% soln. in CH_2Cl_2
(21)	$Sn(SBz)_4$	$+132 \pm 2$	*ca.* 25% soln. in CCl_4
(22)	$Ph_3SnSeMe$	-69 ± 1	*ca.* 30% soln. in CH_2Cl_2
(23)	$Ph_2Sn(SeMe)_2$ [b]	-20 ± 1	*ca.* 30% soln. in CH_2Cl_2
(24)	$PhSn(SeMe)_3$ [c]	-21 ± 1	*ca.* 30% soln. in CH_2Cl_2
(25)	$Sn(SeMe)_4$	-80.5	Neat
(26)	$Me_3SnSCPh_3$	$+67.4 \pm 2$	50% soln. in CH_2Cl_2
(27)	$PhSSnMe_3$	$+91.3 \pm 0.2$	25% soln. in CH_2Cl_2
(28)	$4\text{-}MeC_6H_4SSnMe_3$	$+92.9 \pm 0.2$	25% soln. in CH_2Cl_2
(29)	$4\text{-}Bu^tC_6H_4SSnMe_3$	$+89.7 \pm 0.2$	25% soln. in CH_2Cl_2
(30)	$4\text{-}NH_2C_6H_4SSnMe_3$	$+90.7 \pm 0.2$	25% soln. in CH_2Cl_2
(31)	$4\text{-}ClC_6H_4SSnMe_3$	$+95.1 \pm 0.2$	25% soln. in CH_2Cl_2
(32)	$4\text{-}BrC_6H_4SSnMe_3$	$+98.7 \pm 0.2$	CH_2Cl_2
(33)	$4\text{-}NO_2C_6H_4SSnMe_3$	$+103.7 \pm 0.2$	CH_2Cl_2
(34)	$PhSSnPh_3$	-65.2 ± 1	CH_2Cl_2
(35)	$4\text{-}MeC_6H_4SnPh_3$	-67.4 ± 1	CH_2Cl_2
(36)	$4\text{-}Bu^tC_6H_4SnPh_3$	-66.3 ± 1	CH_2Cl_2
(37)	$4\text{-}NH_2C_6H_4SnPh_3$	-69.2 ± 1	CH_2Cl_2
(38)	$4\text{-}ClC_6H_4SnPh_3$	-64.4 ± 1	CH_2Cl_2
(39)	$4\text{-}NO_2C_6H_4SnPh_3$	-61.8 ± 1	CH_2Cl_2
(40)	$4\text{-}BrC_6H_4SnPh_3$	-63.6 ± 1	CH_2Cl_2
(41)	$4\text{-}MeOC_6H_4SnPh_3$	-65.8 ± 1	CH_2Cl_2
(42)	$(PhS)_2SnMe_2$	$+125.6 \pm 0.1$	10% in CH_2Cl_2
(43)	$(4\text{-}BrC_6H_4S)_2SnMe_2$	$+127.6 \pm 0.2$	10% in CH_2Cl_2
(44)	$(4\text{-}ClC_6H_4S)_2SnMe_2$	$+128.3 \pm 0.2$	15% in CH_2Cl_2
(45)	$(4\text{-}NO_2C_6H_4S)_2SnMe_2$	$+130.8 \pm 0.1$	10% in CH_2Cl_2
(46)	$(4\text{-}NH_2C_6H_4S)_2SnMe_2$	$+121.6 \pm 0.1$	Satd. (*ca.* 5%) in CH_2Cl_2
(47)	$(4\text{-}MeC_6H_4S)_2SnMe_2$	$+123.5 \pm 0.1$	15% in CH_2Cl_2
(48)	$(4\text{-}Bu^tC_6H_4S)_2SnMe_2$	$+124.7 \pm 0.1$	10% in CH_2Cl_2
(49)	$PhSCH_2SnPh_3$	-118.0 ± 0.5	30% in CH_2Cl_2
(50)	$4\text{-}NO_2C_6H_4SCH_2SnPh_3$	-118.2 ± 0.5	20% in CH_2Cl_2
(51)	$4\text{-}ClC_6H_4SCH_2SnPh_3$	-118.5 ± 0.5	15% in CH_2Cl_2
(52)	$4\text{-}BrC_6H_4SCH_2SnPh_3$	-118.5 ± 1	20% in CH_2Cl_2
(53)	$4\text{-}Bu^tC_6H_4SCH_2SnPh_3$	-119.0 ± 0.5	20% in CH_2Cl_2
(54)	$4\text{-}MeOC_6H_4SCH_2SnPh_3$	-119.5 ± 1.5	15% in CH_2Cl_2
(55)	$4\text{-}NH_2C_6H_4SCH_2SnPh_3$	-120.7 ± 0.5	15% in CH_2Cl_2
(56)	$PhSnMe_3$	-28.6 ± 0.2	20% in CH_2Cl_2
(57)	$4\text{-}MeC_6H_4SnMe_3$	-28.3 ± 0.2	20% in CH_2Cl_2
(58)	$4\text{-}MeOC_6H_4SnMe_3$	-27.4 ± 0.2	20% in CH_2Cl_2
(59)	$(PhSe)_4Sn$	-135 ± 2	Sat. soln. in CH_2Cl_2
(60)	$(Bu^tSe)_4Sn$ [d]	-262 ± 1	Sat. soln. in CH_2Cl_2
(61)	$MeSnI_3$	-699.5 ± 1	Sat. soln. in CCl_4

[a] To low field of Me_4Sn. [b] $\delta(^{77}Se) = 282$ p.p.m. to high field of Me_2Se. [c] $\delta(^{77}Se) = 217$ p.p.m. to high field of Me_2Se. [d] $\delta(^{77}Se) = 326$ p.p.m. to high field of Me_2Se.

TABLE 3

^{119}Sn Chemical shifts and other data (J in Hz) for tin-containing species present in mixtures [a]

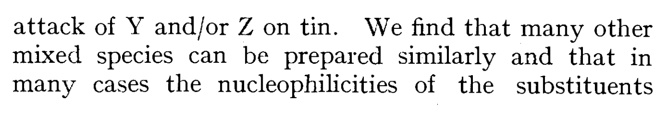
Initial components	Species identified [b]	δ(^{119}Sn)/p.p.m.[c]	Other n.m.r. data [d]
(MeSe)$_4$Sn–(MeS)$_4$Sn 20% in CH$_2$Cl$_2$	(MeS)$_3$SnSeMe *	+101 ± 2	δ(H)(MeS) 2.33; ^3J(Sn···H) *ca.* 65 δ(H)(MeSe) 2.22; δ(Se)− 149 ± 2; ^3J(Sn···H) *ca.* 57
	(MeS)$_2$Sn(SeMe)$_2$ *	+43 ± 2	
	MeSSn(SeMe)$_3$ *	−21 ± 3	
(Bu^{t}Se)$_4$Sn–(MeS)$_4$Sn 30% in C$_6$H$_6$	(MeS)$_4$Sn		δ(H)(MeS) 2.00; ^3J(Sn···H) 66.7
	(MeS)$_3$SnSeBu^t *	+80.6 ± 1.5	δ(H)(MeS) 2.10; ^3J(Sn···H) 65.2; δ(H)(Bu^{t}Se) 1.56; δ(Se) −226.9
	(MeS)$_2$Sn(SeBu^t)$_2$ *	−18.2 ± 1.5	δ(H)(MeS) 2.17; ^3J(Sn···H) 64.0; δ(H)(Bu^{t}Se) 1.60; δ(Se) −258.3
	MeSSn(SeBu^t)$_3$ *	−129.5 ± 1.5	δ(H)(MeS) 2.25; ^3J(Sn···H) 63.4; δ(H)(Bu^{t}Se) 1.64; δ(Se) −291.2
	Sn(SeBu^t)$_4$		δ(H)(Bu^{t}Se) 1.68; δ(Se) −325.7
(PhSe)$_4$Sn–(MeS)$_4$Sn 40% in CH$_2$Cl$_2$	(MeS)$_4$Sn	+158 ± 5	δ(H)(MeS) 2.30; ^3J(Sn···H) 66 ± 2
	(MeS)$_3$Sn(SePh) *	+87 ± 2	δ(H)(MeS) 2.20; ^3J(Sn···H) 66 ± 2
	(MeS)$_2$Sn(SePh)$_2$ *	+12.5 ± 1	δ(H)(MeS) 2.09; ^3J(Sn···H) 66 ± 2
	MeSSn(SePh)$_3$ *	−61 ± 1	δ(H)(MeS) 2.00; ^3J(Sn···H) 66 ± 2
(Bu^{t}S)$_4$Sn–(MeS)$_4$Sn 15% in CH$_2$Cl$_2$	(MeS)$_3$SnSBu^t *	+127 ± 1	δ(H)(MeS) 2.315; ^3J(Sn···H) 66.5 δ(H)(Bu^{t}S) 1.55; ^4J(Sn···H) 4.85
	(MeS)$_2$Sn(SBu^t)$_2$ *	+92 ± 1	δ(H)(MeS) 2.325; ^3J(Sn···H) 66.25
	MeSSn(SBu^t)$_3$ *	+58 ± 2	δ(H)(MeS) 2.355; ^3J(Sn···H) 66.1
(PhS)$_4$Sn–(MeS)$_4$Sn 15% in CH$_2$Cl$_2$	(MeS)$_3$SnSPh *	+131 ± 5	δ(H)(MeS) 2.20; ^3J(Sn···H) 66
	(MeS)$_2$Sn(SPh)$_2$ *	+104 ± 5	δ(H)(MeS) 2.10; ^3J(Sn···H) 68
	MeSSn(SPh)$_3$ *	+77 ± 5	δ(H)(MeS) 2.02; ^3J(Sn···H) 70.5
SnI$_4$–(MeS)$_4$Sn 10% in CH$_2$Cl$_2$ [e]	(MeS)$_3$SnI *	−40.5 ± 3	δ(H)(MeS) 2.25br; ^{3}J(Sn···H) not resolved.
	(MeS)$_2$SnI$_2$ *	−399 ± 2	
	MeSSnI$_3$ *	−950 ± 6	
(PhCH$_2$S)$_4$Sn–(MeS)$_4$Sn 5% in CH$_2$Cl$_2$	(MeS)$_4$Sn	130—160 [f]	δ(H)(MeS) 2.41 [g] Both ^3J(Sn···H) *ca.* 60 ± 10 (broad and not well resolved)
	(MeS)$_3$SnSCH$_2$Ph *		δ(H)(MeS) 2.36 [g]; δ(H)(ArCH_2S) 4.21 [g]
	(MeS)$_2$Sn(SCH$_2$Ph)$_2$ *		δ(H)(MeS) 2.32 [g]; δ(H)(ArCH_2S) 4.15 [g]
	MeSSn(SCH$_2$Ph)$_3$ *		δ(H)(MeS) 2.23 [g]; δ(H)(ArCH_2S) 4.09 [g] δ(H)(ArCH_2S) 4.02
SnI$_4$–(Bu^{t}S)$_4$Sn 30% in CH$_2$Cl$_2$	(Bu^{t}S)$_4$Sn	+24.4 ± 1	δ(H)(Bu^{t}S) 2.599; ^4J(Sn···H) 4.8
	(Bu^{t}S)SnI *	−210.5 ± 2	δ(H)(Bu^{t}S) 2.613; ^4J(Sn···H) 6.0
	(Bu^{t}S)$_2$SnI$_2$ *	−565 ± 2	δ(H)(Bu^{t}S) 2.633; ^4J(Sn···H) 7.1
	Bu^{t}SSnI$_3$ *	−1 065 ± 2	δ(H)(Bu^{t}S) 2.653; ^4J(Sn···H) 9.3
Sn(NEt$_2$)$_4$–(MeS)$_4$Sn [h] 25% in CH$_2$Cl$_2$	(MeS)$_4$Sn	+163 ± 5	SCH$_3$ (s) and NCH$_2$ (q) broad –SCH$_3$ sharpened by ν(Sn) corresponding to δ(Sn) = +163, +93, and −80.5 p.p.m. –NCH$_2$ sharpened by ν(Sn) corresponding to δ(Sn) = +93 and −80.5 p.p.m. only
	(MeS)$_3$NEt$_2$ *	+93 ± 5	
	?	−80.5 ± 5	
MeSnI$_3$–MeSn(SBu^t)$_3$ 10% in CH$_2$Cl$_2$	MeSnI$_3$	−703 ± 5	δ(H)(MeSn) 2.59; ^2J(Sn···H) 76
	MeSnI$_2$(SBu^t) *	−321 ± 2	δ(H)(MeSn) 2.26; ^2J(Sn···H) 72.5
	MeSnI(SBu^t)$_2$ *	−84 ± 4	δ(H)(MeSn) 1.80; ^2J(Sn···H) 66 ± 1.5
MeSnI$_3$–MeSn(SEt)$_3$ 10% in CH$_2$Cl$_2$	MeSnI$_2$(SEt) *	−274 ± 2	δ(H)(MeSn) 1.90br; ^2J(Sn···H) not resolved
	MeSnI(SEt)$_2$ *	−2 ± 5	δ(H)(MeSn) 1.37; ^2J(Sn···H) 65 ± 5
MeSnI$_3$–MeSn(SPh)$_3$ 10% in CH$_2$Cl$_2$	MeSnI$_3$	−698 ± 2	δ(H)(MeSn) 2.35; ^2J(Sn···H) 75.5
	MeSnI$_2$(SPh) *	−294 ± 1	δ(H)(MeSn) 1.71; ^2J(Sn···H) 69.5
	MeSnI(SPh)$_2$ *	−45 ± 2	δ(H)(MeSn) 1.10; ^2J(Sn···H) 66
	MeSn(SPh)$_3$	+100 ± 5	δ(H)(MeSn) 0.50; ^2J(Sn···H) 62.2
MeSnI$_3$–MeSnCl$_3$ 20% in C$_6$H$_6$	MeSnI$_3$	−690 ± 3	δ(H)(MeSn) 1.55sh; ^2J(Sn···H) 75 ± 1
	MeSnI$_2$Cl *	−436 ± 3	δ(H)(MeSn) 1.15broader; ^2J(Sn···H) 80 ± 2
	MeSnICl$_2$ *	−202 ± 5	δ(H)(MeSn) 0.67br; ^2J(Sn···H) *ca.* 90; satellite perturbed by two frequencies corresponding to δ(Sn) values given
	MeSnCl$_3$	+17.5 ± 5	
MeSnI$_3$–(Me$_2$SnS)$_3$ 20% in CH$_2$Cl$_2$	Me$_2$SnI$_2$	−155.3 ± 1	δ(H)(MeSn) 1.71; ^2J(Sn···H) 63.5
Me$_2$SnI$_2$–Me$_2$SnCl$_2$ 20% in C$_6$H$_6$	Me$_2$SnI$_2$	−152 ± 3	δ(H)(MeSn) 0.85sh; ^2J(Sn···H) 61; satellite perturbed by three frequencies corresponding to three δ(Sn) values given
	Me$_2$SnICl *	+15 ± 5	
	Me$_2$SnCl$_2$	+131 ± 5	
Me$_2$SnI$_2$–Me$_2$Sn(SPr^i)$_2$ 50% in CH$_2$Cl$_2$	Me$_2$SnI(SPr^i) *	+26 ± 2	δ(H)(MeSn) 1.67; ^2J(Sn···H) 60
	?	+158 ± 2	δ(H)(MeSn) 0.70; ^2J(Sn···H) 57; increased intensity on addition of more Me$_2$Sn(SPr^i)$_2$ but otherwise unchanged.
Me$_2$SnI$_2$–Me$_2$Sn(SPh)$_2$ 20% in CH$_2$Cl$_2$	Me$_2$SnI(SPh) *	+28 ± 2	δ(H)(MeSn) 1.10; ^2J(Sn···H) 63 ± 2
	?	+148 ± 5	δ(H)(MeSn) 0.60; ^2J(Sn···H) *ca.* 60; δ(Sn) became +126 on addition of more Me$_2$Sn(SPh)$_2$
Me$_2$SnI$_2$–(Me$_2$SnS)$_3$ 30% in CH$_2$Cl$_2$–CCl$_4$	Me$_2$SnI$_2$	−167.5 ± 5	δ(H)(MeSn) 1.72; ^2J(Sn···H) 57 ± 2
	(Me$_2$SnI)$_2$S *	+13.5 ± 5	δ(H)(MeSn) 1.37; ^2J(Sn···H) satellites hidden
	(Me$_2$SnS)$_3$	+129.5 ± 5	δ(H)(MeSn) 0.93; ^2J(Sn···H) 63 ± 2

[a] H, Se, and Sn parameters refer to ^{1}H, ^{77}Se, and ^{119}Sn isotopes respectively. [b] * Indicates previously unreported species. [c] Relative to Me$_4$^{119}Sn = 0. [d] Chemical shift given in p.p.m. δ(^{77}Se) relative to Me$_2$^{77}Se = 0; δ(^{1}H) relative to (CH$_3$)$_4$Si = 0. [e] Solution deposited intractable orange crystalline solid on standing. [f] ^{119}Sn Resonances not well resolved. [g] Assigned by observing changes in proportions on further addition of one initial component. [h] Similar experiment on the (MeS)$_4$Sn–(Ph$_2$P)$_4$Sn system showed only one broad signal for the MeS protons which was not perturbed by ^{31}P or ^{119}Sn frequencies and the solution quickly deposited a yellow solid on standing.

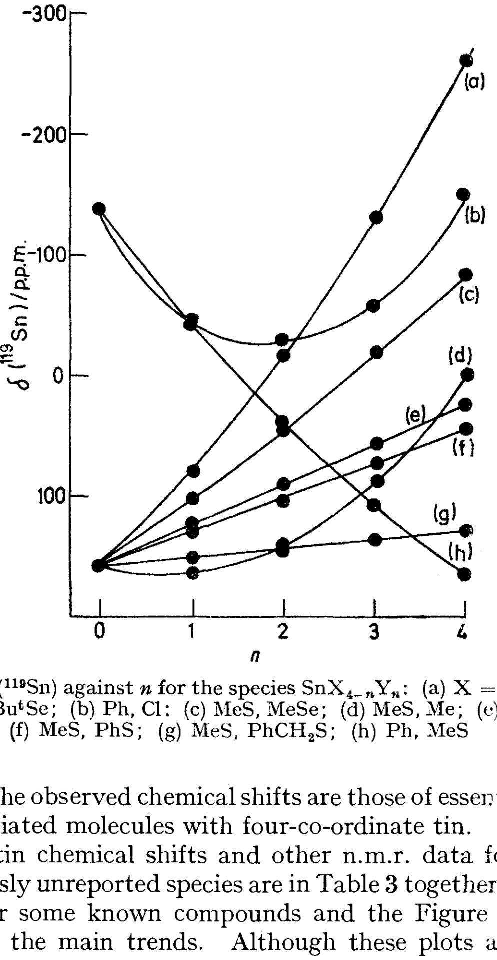
$(4\text{-}XC_6H_4S)_2SnMe_2$. Although these trends are in the direction predicted by dominance of the tin shielding by the diamagnetic contribution[11] it is difficult to reconcile their relative magnitudes with any simple correlation between $\delta(^{119}Sn)$ and the electron density on the tin atom as required by the diamagnetic term. The paramagnetic term in the expression for the tin shielding depends upon the relative electronic imbalance in the bonds to tin and will therefore be a maximum when the tin atom has two substituents with electronegativities which are substantially different from those of the other two substituents.[12] Thus in the species $(4\text{-}XC_6H_4S)_2SnMe_2$ this imbalance will be larger than in $4\text{-}XC_6H_4SSnMe_3$ and a change in the nature of X will have a proportionately smaller effect. Additionally the relatively high polarizability of the $4\text{-}XC_6H_4S$ group will mitigate the effects of a change in X in the other benzenethiolate group in the former series of molecules. This latter effect can also account for the reduced sensitivity to the nature of X in the series $4\text{-}XC_6H_4SSnPh_3$: the relatively high mobility of the electrons of the phenyl groups (possibly but not necessarily enhanced by π overlap between tin and these groups) will tend to offset any electronic imbalance in bonds to tin arising from a change in the effective electronegativity of a substituent.

Intercalation of a methylene group between tin and sulphur in this type of compound [(55)—(69)] reduces the dependence of $\delta(^{119}Sn)$ upon the nature of X to less than the experimental error. However, the presence of a sulphur atom between tin and the substituted phenyl group has no such insulating effect and molecules $4\text{-}XC_6H_4SnMe_3$ [(56)—(58)] have tin chemical shifts which are if anything less sensitive to the nature of X than the thiolate derivatives. This may indicate that there is significant π interaction between sulphur and tin.

The tin shielding of compounds SnX_nY_{4-n} shows a complex pattern of variation with the value of n, with marked deviations from linearity in many cases. In the earliest work[13] on tin-119 n.m.r., equilibrated mixtures of tin tetrahalides were examined and it was found that mixed species had lifetimes which were long on the n.m.r. time scale (note that the tin chemical shifts extended over several thousands of Hz) and linear additivity relationships were found to reproduce the observed chemical shifts. These redistribution reactions are generally thought to involve intermediate states with five-co-ordinate tin as in (1) and thus proceed *via* nucleophilic attack of Y and/or Z on tin. We find that many other mixed species can be prepared similarly and that in many cases the nucleophilicities of the substituents are sufficiently low to give life-times long enough for separate resonances in the proton spectrum (the relevant portion of which extends over some tens of Hz) as well as in the tin-119 spectrum. Thus in most cases we were able to get tin chemical shifts by standard $^1H\text{-}\{^{119}Sn\}$ double resonance experiments which also served to confirm assignments by unequivocally relating resonances in the tin and proton spectra. Additionally in the present work few of the substituents were sufficiently basic towards tin for stable five-co-ordinate species to be formed [except presumably in the case of the $(MeS)_4Sn\text{-}(Et_2N)_4Sn$ system in which the highfield tin-119 chemical shift of −80.5 p.p.m. is probably due to a five-co-ordinate species] and so the observed chemical shifts are those of essentially unassociated molecules with four-co-ordinate tin.



(1)



Plot of $\delta(^{119}Sn)$ against n for the species $SnX_{4-n}Y_n$: (a) X = MeS, Y = Bu^tSe; (b) Ph, Cl; (c) MeS, MeSe; (d) MeS, Me; (e) MeS, Bu^tS; (f) MeS, PhS; (g) MeS, $PhCH_2S$; (h) Ph, MeS

The tin chemical shifts and other n.m.r. data for 37 previously unreported species are in Table 3 together with data for some known compounds and the Figure summarizes the main trends. Although these plots are of apparently widely differing appearance they may be characterized by two parameters: the difference in tin chemical shift of the extreme components (*i.e.* for n = 0 and 4) and the extent of the departure from linearity. The latter parameter may be obtained by subtracting from each value of $\delta(^{119}Sn)$ for each series $SnX_{4-n}Y_n$ an amount $n\Delta/4$ where $\Delta = [\delta(^{119}Sn)_{n=4} - \delta(^{119}Sn)_{n=0}]$. When this is done for the series $Me_{4-n}Sn(SMe)_n$ an almost symmetrical curve is obtained with a maximum deviation from linearity (very close to $n = 2$) of 62.5 p.p.m. to low

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[11] W. E. Lamb, *Phys. Rev.*, 1941, **60**, 817.

[12] C. J. Jameson and H. S. Gutwosky, *J. Chem. Phys.*, 1964, **40**, 1714.

[13] J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 326.

field. Furthermore similar treatment of the data for the series $Me_{4-n}Sn(SR)_n$ (R = Et, Pr^i, Bu^t, or Ph) yields a set of curves which are exactly (to ± 1 p.p.m.) superposable upon that obtained for R = Me and which show that the apparently large differences in curvature of these plots associated with different alkyl groups are merely consequences of the mode of presentation of the data. The series $Ph_{4-n}Sn(SR)_n$ give another set of superposable curves with a maximum deviation from linearity (at $n = 2$) of 25 p.p.m. to low field. This smaller value compared with the methyl compounds may be attributed partly to the ability of the phenyl groups to mitigate the effects of electron movements as discussed earlier for the $4\text{-}XC_6H_4SSnPh_3$ compounds, and partly to the smaller difference in electron-withdrawing power between phenyl and sulphur.

TABLE 4

Deviations from linearity of plots of $\delta(^{119}Sn)$ against n in the series $SnX_{4-n}Y_n$

X/Y	Deviation/p.p.m. at $n = 2$	$\frac{\delta(SnX_4) - \delta(SnY_4)}{\text{p.p.m.}}$
Me/SR	62	−160 (R = Me)
Me/Cl	212	+150
Me/I	691	+1 701
Me/SeMe	107	+80.5
Ph/SR	25	−300 (R = Me)
Ph/Cl	112	+13
MeS/Bu^t	−1	+134
MeS/MeSe	3	+240
MeS/Bu^tSe	33	+422
MeS/I	369	+1 861
Bu^tS/I	273	+1 727

Treatment of the data for other sets of mixed tin species $SnX_{4-n}Y_n$ in this manner gives the maximum deviations from linearity (at or near $n = 2$) listed in Table 4. Data for species $MeSnX_{3-n}Y_n$ can be similarly processed.

The expression of Jameson and Gutowsky [12] for the paramagnetic contribution to the shielding suggests that these deviations should depend upon the degree of electron imbalance in the bonds to tin and hence upon the electronegativity difference between X and Y. Furthermore their equation predicts that the deviation from linearity should be a maximum at $n = 2$. Although this is clearly an important factor in certain cases, *e.g.* X = Me, Y = SR; X = MeS, Y = Bu^tS; it is also clear that other factors are involved. Thus for example, the deviation for Me/I is much greater than for Me/Cl and the influence of a Bu^t group is not the same when attached to sulphur and selenium. It is also noteworthy that in cases for which the electronegativity difference is relatively small (*e.g.* Me/Ph or Et/$-C{\equiv}CH$) accurately linear plots are obtained.[14] With bulky polarizable substituents such as I or Se abnormal deviations may arise. The main value of the above approach is that it makes apparent large deviations which had previously been obscured and emphasizes similarities in behaviour of certain sets of molecules.

The other parameter, the difference in $\delta(^{119}Sn)$ for SnX_4 and SnY_4, will depend upon the electronegativities of X and Y which will affect the diamagnetic term. However, the size of the substituent is also important; although as discussed elsewhere the neighbouring atom diamagnetic contribution appears to be unable to account entirely for the high field shifts associated with large substituents. The limited data currently available for silicon and lead shielding [15] suggests that this ' bulky atom ' effect involves the paramagnetic term.

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