Magnetic Double Resonance Studies of Some Methyltin Alkane- and Benzene-thiolates

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^{1}H, ^{13}C, and ^{119}Sn n.m.r. parameters for the series of methyltin alkane- and benzene-thiolates $Me_{4-n}Sn(SR)_n$, where n = 1—4, and R = Me, Et, Pr^i, Bu^t, and Ph, are reported and discussed in terms of the electronic structures of the molecules, with particular reference to the factors affecting the ^{119}Sn chemical shift.

THE factors which determine the magnetic shielding of the heavier nuclei are not completely understood, and it is important to have experimental data for series of related molecules. We report here measurements in the trends of six n.m.r. parameters (including ^{119}Sn chemical shifts) of some methyltin alkane- and benzene-thiolates, $Me_{4-n}Sn(SR)_n$ (n = 1—4; R = Me, Et, Pr^i, Bu^t, and Ph), which show no appreciable tendency for auto-association in the liquid phase, unlike the analogous alkoxides.[1,2] Some of these thiolates have not been reported previously.

Recently, the ^{119}Sn and ^{13}C chemical shifts of the

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[1] J. D. Kennedy, W. McFarlane, P. J. Smith, R. F. M. White, and L. Smith, *J.C.S. Perkin II*, 1973, 1785.

[2] J. D. Kennedy, W. McFarlane, and D. S. Rycroft, unpublished results for $Me_{4-n}Sn(OR)_n$.

methyltin methanethiolates have been reported;[3] this work extended an earlier study of the proton parameters.[4] Other observations on the ^{1}H n.m.r. of Group IVB–sulphur bonded compounds have been made,[5-8] and the methyltin methaneselenolates have also been examined.[9]

EXPERIMENTAL

Preparation of Methyltin Alkane- and Benzene-thiolates.—All were prepared on a scale of *ca.* 10 mmol of organotin compound by the same method as described for the methyltin methaneselenolates [9] but by use of the appropriate thiol instead of methaneselenol. Products were purified by repeated distillation under reduced pressure, and yields were essentially quantitative. Physical and analytical data for new compounds are given in Table 1. The tri- and tetra-thiolates were stored and manipulated under dry nitrogen.

TABLE 1

Physical properties and analytical data for new compounds [a]

Compound	B.p. (°C at mmHg)	Calc. (%)			Found (%)		
		C	H	S	C	H	S
$Me_2Sn(SPr^i)_2$	60—62 at 0·20	32·1	6·75	21·4	32·1	6·65	21·2
$MeSn(SPr^i)_3$	79—81 at 0·008	33·4	6·75	26·75	33·2	6·65	26·9
$Me_2Sn(SBu^t)_2$	63—65 at 0·01	36·7	7·4	19·6	37·0	7·35	19·35
$MeSn(SBu^t)_3$	95—97 at 0·007 [b]	38·9	7·5	24·0	38·8	7·5	23·8
$MeSn(SPh)_3$	196—198 at 0·01 [c]	49·5	3·95	20·8	49·9	3·9	20·65

[a] Physical data for other methyltin thiolates are tabulated by H. Schumann, I. Schumann-Ruidisch, and M. Schmidt, 'Organotin Compounds,' ed. A. K. Sawyer, Marcel Dekker, New York, 1971, vol. 2. [b] M.p. 53—54°. [c] With apparent decomposition; analytical data given for crude compound before distillation.

N.m.r. Measurements.—N.m.r. measurements (Table 2) were made on neat liquids (except where indicated) at 24° and using *ca.* 5% tetramethylsilane as internal standard. The multiple resonance technique and equipment have been described.[9] Tin chemical shifts are quoted relative to $Me_4{}^{119}Sn = 0$, carbon chemical shifts relative to $Me_3Si^{13}CH_3 = 0$, and both increase algebraically with decreased nuclear shielding.

RESULTS AND DISCUSSION

Preparation and Properties.—The methyltin thiolates were prepared by the action of triethylamine on ethereal solutions of the methyltin chloride and the appropriate thiol. The products were generally liquids or low-melting solids (*e.g.* Table 1). The methyltin trithiolates and tin tetrathiolates are not indefinitely stable in air, but are susceptible to slow atmospheric hydrolysis. The dimethyl and trimethyl compounds are more stable.

Unlike their oxygen analogues [1,2,10] the tin thiolates are unassociated in the liquid phase: the ^{119}Sn chemical shift does not move to lower applied field on dilution in non-nucleophilic solvents or on heating, which confirms monomeric behaviour.[1,2] The absence of auto-association is due to a combination of the low basicity of the sulphur lone-pair electrons towards tin(IV) [11] and the low Lewis acidity of tin when bound to alkyl groups and/or simple mercaptide ligands. This is demonstrated by the data in Table 3.

The electron distribution about the tin atom is modified by an increase in co-ordination number; this generally results in a considerable shift to high field of the ^{119}Sn resonance together with, in methyltin compounds, a substantial increase in $|^2J(Sn\cdots H)|$. In dynamic ligand–associative equilibria, the observed values of $\delta(^{119}Sn)$ and $^2J(Sn\cdots H)$ are time-averages of the discrete values for the various species present. Alkyltin halides form strong complexes with dimethyl sulphoxide (DMSO),[12] and the parameters in Table 3 for the methyltin chlorides in this as solvent therefore correspond to the extreme species $Me_3SnCl,DMSO$, $Me_2SnCl_2,2DMSO$, and $MeSnCl_3,2DMSO$. These values differ significantly from those reported in the literature,[13] which were measured using solutions of the complexes in dichloromethane; this is a manifestation of the known dissociation [12,14,15] of many organotin complexes in neutral solvents. The ^{119}Sn chemical shift of $MeSnCl_3,2DMSO$ (−487 p.p.m.) is the lowest so far reported for a neutral organotin species, but is of the order expected for a six-co-ordinate monoalkyltin compound.[1,2]

By contrast, no significant interaction occurs between dimethyl sulphide and methyltin trismethanethiolate. This organotin thiolate does however show weak co-ordinative interaction with the stronger Lewis base dimethyl sulphoxide, as does, conversely, dimethyl sulphide with the progressively stronger Lewis acids trimethyltin chloride, dimethyltin dichloride, and methyltin trichloride. As expected, the co-ordinative interaction increases in this order; the trichloride forms an unstable, solid 1 : 1 adduct.

N.m.r. Parameters.—As *n* increases in the series $Me_{4-n}Sn(SR)_n$ the coupling $^1J(^{13}C-H)$ in the *Sn*-methyl groups also increases. This can be attributed [16-18] to

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[7] E. W. Abel and D. B. Brady, *J. Organometallic Chem.*, 1968, **11**, 145.

[8] A. J. Oliver and W. A. G. Graham, *J. Organometallic Chem.*, 1969, **19**, 17.

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[10] P. J. Smith, R. F. M. White, and L. Smith, *J. Organometallic Chem.*, 1972, **40**, 341.

[11] I. P. Gol'dstein, E. N. Gur'yanova, and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, 1961, **138**, 1099; I. R. Beattie, *Quart. Rev.*, 1963, **17**, 382.

[12] (*a*) T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, 1965, **87**, 5015; 1966, **88**, 3921, 5730; (*b*) H. G. Langer and A. H. Blut, *J. Organometallic Chem.*, 1966, **5**, 288; (*c*) W. Kitching, *Tetrahedron Letters*, 1966, 3689.

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[16] W. McFarlane, *Quart. Rev.*, 1969, **23**, 187.

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[18] D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, 1965, **87**, 3994.

an increase in the effective nuclear charge of carbon and/or diversion of *s* character from the C–Sn bonds as a result of inductive electron withdrawal from tin by the electronegative thiolate groups. The differences in electron density on tin for different alkyl groups R are too small to have an observable effect upon this coupling constant, but it is appreciably larger for R = Ph. The tin–proton coupling constants exhibit similar behaviour but there appears to be a dependence upon the hybridisation of the tin atom in addition to its charge, because the changes in $^2J(^{119}\mathrm{Sn}\cdots\mathrm{H})$ as n varies are affected by the bulk of R. The large spread of values observed for $^3J(^{119}\mathrm{Sn}\cdots\mathrm{H})$ in the thiolate groups suggests that, in addition to the foregoing, conformational effects are also important.

TABLE 2

N.m.r. parameters of methyltin alkane- and benzene-thiolates (neat liquids)

Compound	$\delta(^{119}\mathrm{Sn})$ (p.p.m.)	$\delta(^{13}C\mathrm{H}_3)$ (p.p.m.)	$\delta(\mathrm{C}^1H_3\mathrm{Sn})$ (p.p.m.)	$^2J(\mathrm{Sn{-}H})$/Hz	$^3J(\mathrm{Sn{-}H})$/Hz	$^1J(^{13}C{-}^1H_3\mathrm{Sn})$/Hz
$\mathrm{Me_4Sn}$	0	−8·6	0·04	53·9 ± 0·2		127·8 ± 0·2
$\mathrm{Me_3SnSMe}$	+90 [a]	−4·7 [b]	0·35 [a]	56·9 [c]	37·5 [c]	135 [d]
$\mathrm{Me_2Sn(SMe)_2}$	+144 [a]	−1·9 [b]	0·65 [a]	61·2 [c]	44·2 [c]	135 [d]
$\mathrm{MeSn(SMe_3)}$	+167 [a]	+1·7 [b]	0·94 [a]	66·6 [c]	56·7 [c]	135 [d]
$\mathrm{Sn(SMe)_4}$	+165 [a]				66·0 [c]	
$\mathrm{Me_3SnSEt}$	+78	−4·35	0·41	56·7 ± 0·1	33·4 ± 0·5	129·8 ± 0·8
$\mathrm{Me_2Sn(SEt)_2}$	+127	−0·8	0·67	59·85 ± 0·15	41·3 ± 0·2	133·1 ± 0·6
$\mathrm{MeSn(SEt)_3}$	+144	+2·85	0·94	65·2 ± 0·3	54·0 ± 0·3	134·3 ± 1·0
$\mathrm{Sn(SEt)_4}$	+138				67·2 ± 0·3	
$\mathrm{Me_3SnSPr^i}$	+69·5	−4·25	0·38	56·7 ± 0·2	28 ± 2 [e]	130·2 ± 0·4
$\mathrm{Me_2Sn(SPr^i)_2}$	+110	−0·15	0·66	59·2 ± 0·1	34·8 ± 0·4	132·3 ± 0·3
$\mathrm{MeSn(SPr^i)_3}$	+119·5	+4·05	0·93	64·1 ± 1·5	41·9 ± 0·7	134·0 ± 0·3
$\mathrm{Sn(SPr^i)_4}$	+106·5				58·9 ± 0·6	
$\mathrm{Me_3SnSBu^t}$	+55·5	−2·7	0·40	56·4 ± 0·3		129·2 ± 0·5
$\mathrm{Me_2Sn(SBu^t)_2}$	+75	+2·25 [f]	0·67	58·6 ± 0·2	[g]	132·0 ± 0·4
$\mathrm{MeSn(SBu^t)_3}$	+65	+8·5	1·01	63·0 ± 0·8	[h]	134·0 ± 0·8
$\mathrm{Sn(SBu^t)_4}$ [i]	+26 [i]				[i]	
$\mathrm{Me_3SnSPh}$	+90·5	−3·6	0·29	55·5 ± 0·2		130·8 ± 0·4
$\mathrm{Me_2Sn(SPh)_2}$ [j]	+122·5	−0·45	0·37	59·9 ± 0·2		133·8 ± 0·2
$\mathrm{MeSn(SPh)_3}$	+101·5	+1·2	0·30	62·2 ± 0·2		137·6 ± 0·6
$\mathrm{Sn(SPh)_4}$ [k]	+44					

[a] Values from ref. 3. [b] Values from ref. 3 corrected to $\delta(\mathrm{Me_4Si}) = 0$. [c] Values from ref. 7, which are essentially in agreement with those from ref. 3. [d] Values from ref. 4. [e] Obtained from fine structure of $^{119}\mathrm{Sn}$ spectrum. [f] 50% Solution in $\mathrm{CCl_4}$ gives +1·85 p.p.m. [g] $^4J(\mathrm{Sn{-}H})$ 3·4 Hz. [h] $^4J(\mathrm{Sn{-}H})$ 4·2 Hz; 50% solution in $\mathrm{CCl_4}$. [i] $^4J(\mathrm{Sn{-}H})$ 4·9 Hz; saturated $\mathrm{CCl_4}$ solution. [j] Measurements made on supercooled liquid. [k] Saturated solution in $\mathrm{CH_2Cl_2}$.

TABLE 3

N.m.r. parameters of methyltin trismethanethiolate and methyltin chlorides in dimethyl sulphide and dimethyl sulphoxide

Solvent	Compound	$\mathrm{MeSn(SMe)_3}$	$\mathrm{MeSnCl_3}$	$\mathrm{Me_2SnCl_2}$	$\mathrm{Me_3SnCl}$
$\mathrm{CH_2Cl_2}$ or $\mathrm{CCl_4}$	δ (p.p.m.)	+167 [a]	+19 [b]	+137 [b]	+166 [b]
	^2J/Hz	66·6	96·9 [c]	68·9 [c]	58·2 [c]
$\mathrm{Me_2S}$	Conc.	30% v/v	23 mol % [d]	6 mol %	14 mol %
	δ (p.p.m.)	+160	−167	+50	+126
	^2J/Hz	66·4	108	74·05	61·5
$\mathrm{Me_2SO}$	Conc.	30% v/v [e]	Saturated	Saturated	8·5 mol %
	δ (p.p.m.)	+103	−457	−246	−3
	^2J/Hz	75·2	132·5	113	69·5

[a] Value taken from ref. 3. [b] Values taken from A. G. Davies, P. G. Harrison, J. D. Kennedy, T. N. Mitchell, R. J. Puddephatt, and W. McFarlane, *J. Chem. Soc.* (*C*), 1969, 1136. [c] Values taken from H. G. Kuivila, J. D. Kennedy, R. Y. Tien, I. J. Tyminski, F. L. Pelczar, and O. R. Khan, *J. Org. Chem.*, 1971, **36**, 2083. [d] Crystals deposited on partial evaporation of this solution were identified as $\mathrm{MeSnCl_3,Me_2S}$, but these decomposed in the absence of an excess of the sulphide. [e] $^3J(\mathrm{Sn}\cdots\mathrm{H})$ not apparent in $\mathrm{Me_2SO}$ solution.

The reductions in shielding of the *Sn*-methyl protons and $^{13}\mathrm{C}$ nuclei by *ca.* 0·3 and 3·5 p.p.m. respectively per unit of n are also about what would be expected to accompany a reduction of electron density on a polarizable atom such as tin.[19,20] A change in R for a given n has no effect upon the proton shielding in the *Sn*-methyl groups, but affects the $^{13}\mathrm{C}$ shielding in the opposite sense to that expected on the basis of the usual inductive effects of the different alkyl groups. A similar reversed trend in $^{13}\mathrm{C}$ shielding has been observed for the species $(^{13}\mathrm{CH_3})_{4-n}\mathrm{CX}_n$ (X = Cl, Br, or I) which suggests that $p\pi$–$d\pi$ bonding cannot be responsible.[19]

Explanations of the chemical shifts of the heavier nuclei usually assume dominance by the paramagnetic contribution of Ramsey,[21] but it has been claimed

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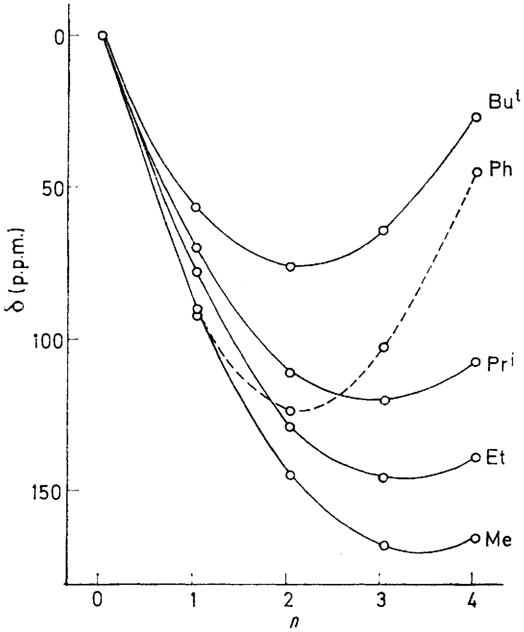
[21] A. Saika and C. P. Slichter, *J. Chem. Phys.*, 1954, **22**, 26.

recently that a neighbouring atom diamagnetic contribution should also be considered.[22] Using the equation of Flygare and Goodisman,[23] and on the basis of idealized bond lengths and interbond angles, and unrestricted rotation about single bonds, the all-atom diamagnetic contributions to the tin shielding due to the groups used in this work are calculated to be Me 36·5, MeS 87·7, EtS 107·3, Pr^iS 126·8, and Bu^tS 146·3 p.p.m. These increase the tin shielding, and small errors in bond lengths and angles should not be serious. In general molecular conformations will be adopted in which bulky groups avoid the tin atom and so these calculated values will be somewhat too large, especially for Bu^tS. When allowance is made for these calculated values the overall spread of ^{119}Sn chemical shifts becomes much larger and the most significant feature, the dip as *n* varies, is not affected. The increase in tin shielding which is observed as R changes from Me to Bu^t can be accounted for by this term. However, the corresponding calculated values for the analogous silicon compounds are all somewhat larger, whereas the observed ^{29}Si chemical shift differences are much smaller,[24] and we believe that any agreement is fortuitous.



δ (^{119}Sn) *versus* *n* in the series $Me_{4-n}Sn(SR)_n$

Replacement of methyl by alkane- or benzene-thiolate affects the tin shielding in a similar manner to replacement by halogen (see Figure), *i.e.*, there is an initial shift to low field, but more extensive substitution reverses this trend. This was not evident from an earlier report, based upon studies of the methanethiolates only.[3] A minimum in the plot of tin shielding *vs.* *n* at *ca.* $n = 2$ can be accounted for by Jameson and Gutowsky's equation[25] for the paramagnetic contribution to the tin shielding which indicates that this term should be a maximum when two of the groups attached to tin are much more electronegative than the other two. The values of $^1J(^{13}C\text{–}H)$ and δ(H) in the *Sn*-methyl groups suggest that changes in R have very little effect upon the total electron density upon the tin atom. However, there are substantial changes in the tin chemical shift which indicate that the electron distribution (*i.e.* $\sigma + \pi$) about tin is varying as R changes from Me to Bu^t. A plot of $\delta(^{119}Sn)$ against the Taft σ^* value of R for $Me_{4-n}Sn(SR)_n$, where R = Me, Et, Pr^i, and Bu^t is linear for $n = 1$, indicating that inductive effects are dominant. For larger *n* the gradients are steeper, as expected, and also become progressively non-linear in a way which indicates that the shielding in the Bu^t compounds is greater than would be expected on purely inductive grounds. This is compatible with there being increased $p\pi\text{–}d\pi$ bonding between tin and sulphur when R = Bu^t so that the paramagnetic term is reduced. There is also the possibility that this $d\pi\text{–}p\pi$ bonding will lead to an increase in the tin shielding by increasing the electron density in tin *d* orbitals. The electron occupancy of these orbitals need not be large for there to be a significant effect; as Table 3 shows, a change in tin orbital occupancy from sp^3 in $MeSnCl_3$ to sp^3d^2 in $MeSnCl_3$,2DMSO leads to an increase in tin shielding of nearly 500 p.p.m. The characteristic curves would then result from a balance between inductive electron withdrawal by the electronegative thiolate groups and increased $p\pi\text{–}d\pi$ back donation as the tin atom becomes more electropositive.

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