^{1}H Nuclear Magnetic Resonance Study of (*d–p*)π Interactions in Stannanes containing Unsaturated Systems

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The proton chemical shift and long range proton–tin coupling constants relative to the methyl group of a number of methylaryl stannanes of general formula $MeSnR_3$, where R is an unsaturated group, were derived. The results show that (*d–p*)π interactions between empty *d* orbitals of tin and the electronic π system of R groups should be small, and in any case the n.m.r. parameters seem to be mainly influenced by an inductive effect from the unsaturated system. Also, the spectra recorded in a solvent which can give co-ordination compounds such as dimethyl sulphoxide, afford no evidence of a major disposal of *d* orbitals for (*d–p*)π interactions. An analogous situation seems to be present in the corresponding compounds of mercury MeHgR. Examination of some *para*-substituted tetra-aryltin compounds indicates that the tin atom also conjugates poorly with *para*-substituents through an aromatic ring.

SEVERAL studies on the ^{1}H n.m.r. parameters of alkylhalogenostannanes have been reported.[1-6] The role of (*d–p*)π interactions between halogens and the tin atom seems to be clear.[6] Redistribution of the *s* orbital of tin in the bonds to carbon could be a rational explanation [1] for the great changes in long range *J*(Sn–C–H) coupling constants found in methyl- and ethyl-halogenostannanes when the number of halogen substituents is increased or on complexing halogenostannanes with good ligands, but a quantitative estimate of hybridization at the tin atom could lead to seriously wrong [7,8] results. Qualitatively speaking, this is supported in theory by the fact that the polarity of the tin–halogen bond [9] makes the *d* orbitals of tin more readily available for π bonding [10] with the doubly-occupied orbitals of the halogens. Some authors [10] are of the opinion that this kind of interaction might be of some importance in the bonding between tin and unsaturated systems. Even if the electronic spectra [11] of arylstannanes and mixed arylalkylstannanes show this contribution to be of slight importance to electronic distribution in these systems, n.m.r. chemical shifts seem to point to a certain amount of conjugation of this kind.[10] According to previous work,[12] it did not seem important to take this effect into account in interpreting the behaviour of long range coupling constants in organometallic derivatives of tin containing heteroaromatic groups. Perturbation due to (*d–p*)π interactions in compounds containing only tin–carbon bonds should be slight, or at least the sensitivity of coupling

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[2] L. Verdonck and G. P. Van der Kelen, *Bull. Soc. chim. belges*, 1967, **76**, 258.

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[6] A. G. Davies, P. G. Harrison, J. D. Kennedy, T. N. Mitchell, R. J. Puddephatt, and W. McFarlane, *J. Chem. Soc.* (*C*), 1969, 1136.

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constants to this interaction should be much lower than that of proton chemical shifts; furthermore, the perturbation attributed to $(d-p)\pi$ interactions may well be due to anisotropy or field effects.

Here, in an attempt to investigate more fully the problem of $(d-p)\pi$ interactions in derivatives where tin can interact with the π electron system of attached rings, we have examined several derivatives of tin containing different unsaturated systems and a methyl group. It is with the n.m.r. parameters of the methyl group that we are immediately concerned in this study. For comparison, some derivatives of mercury will be also taken into account to test the same phenomenon in an element of a different group of the periodic system.

RESULTS AND DISCUSSION

The derivatives chosen for this study are (1) and (2). The ^1H n.m.r. spectra were recorded with particular attention to the methyl group: chemical shifts and long range J(Sn–C–H) and J(Hg–C–H) coupling constants are reported in Tables 1 and 2. Satellite bands for mercury derivatives were found to be broad, especially for the compounds containing furyl groups. This could be accounted for by the quadrupole moment of ^{201}Hg, but we think that the presence of some impurity or exchange phenomena must also play a part.

$MeSnR_3$
(1)
a; R = Me
b; R = $CH{=}CH_2$
c; R = Ph
d; R = 2-Thienyl
e; R = 3-Thienyl
f; R = 2-Furyl
g; R = 3-Furyl

MeHgR
(2)
a; R = Me
b; R = 2-Furyl
c; R = 3-Furyl
d; R = 2-Thienyl
e; R = 3-Thienyl
f; R = Cl
g; R = Br
h; R = I

$Sn(p\text{-}XC_6H_4)_4$
(3)
a; X = OMe
b; X = Me
c; X = D
d; X = Cl

TABLE 1

Chemical shifts and long range coupling constants $J(^{119}Sn–C–H)$ of the methyl group in $MeSnR_3$ measured in $CDCl_3$ and $[^2H_6]$dimethyl sulphoxide (values in parentheses)

Compound	δ_{Me}/p.p.m.	$J(^{119}Sn–C–H)$/Hz
(1a)	0·07 (0·05)	55·8 (55·2)
(1b)	0·25 (0·26)	59·2 (60·4)
(1c)	0·72 (0·76)	57·0 (58·5)
(1d)	0·65 (0·66)	62·8 (66·2)
(1e)	0·74 (0·79)	62·5 (64·1)
(1f)	0·80 (0·81)	69·3 (73·4)
(1g)	0·65 (0·64)	66·0 (67·7)

TABLE 2

Chemical shifts and long range J(Hg–C–H) coupling constants for the methyl group in MeHgR measured in $CDCl_3$

Compound	δ_{Me}/p.p.m.	$J(^{199}Hg–C–H)$/Hz
(2a)	0·33	104·3
(2b)	1·24	190 ± 2
(2c)	1·22	185 ± 3
(2d)	0·70	130·4
(2e)	0·57	123 ± 1
(2f) [a]	1·02	215·2
(2g) [a]	1·06	212·0
(2h)	1·25	192 ± 2

[a] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, in ' Advances in Organometallic Chemistry,' eds. F. G. A. Stone and R. West, Academic Press, New York, vol. 3, 1965. Measured in pyridine solution.

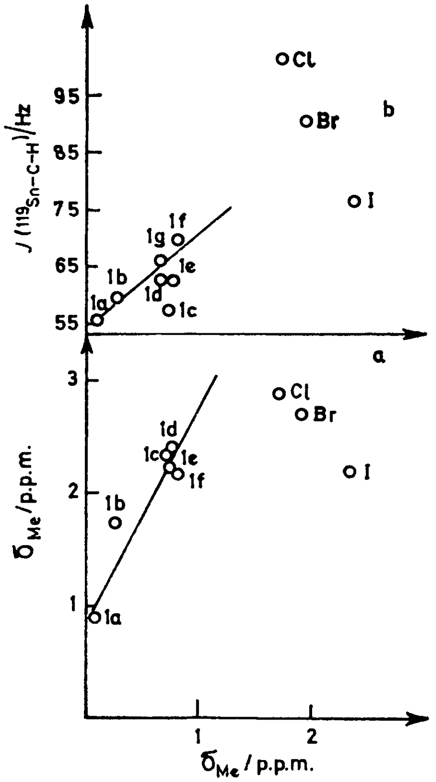

FIGURE 1 Plot a, of δ_{Me} of monosubstituted methanes CH_3R and b, of $J(^{119}Sn–C–H)$ of compounds (1) against δ_{Me} of compounds (1). (The chemical shifts for monosubstituted methanes are from W. Brugel, ' Nuclear Magnetic Resonance Spectra and Chemical Structure,' Academic Press, New York, 1967, and from ref. 14; those for trimethylhalogenostannanes from ref. 13)

In the case of methylhalogenostannanes $MeSnHal_3$, the behaviour of J(Sn–C–H) cannot be simply explained by taking into account the electronegativity of substituents;[7] redistribution of the s orbital in the tin-carbon bonds seems more likely.[13] Furthermore, the behaviour of the chemical shift of the methyl group in these compounds is contrary to that expected if only electronegativity effects are operating. Since, in the compounds here examined, the electronegativity of the R groups is not known, and since the chemical shift of the methyl group in monosubstituted methanes can be roughly assumed to be proportional to the electronegativity of the first atom of the substituent,[14] we have tried to check the importance of electronegativity effects by plotting the chemical shifts, δ_{Me}, in compounds (1) against those of compounds MeR. As shown in Figure 1a, a rough direct proportionality is

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[13] G. Barbieri and F. Taddei, following paper.

[14] L. M. Jackman and S. Sternhell, ' Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon Press, Oxford, 1969, p. 64.

found to substituted methanes, and this could be taken to indicate that in tin compounds containing only tin-carbon bonds the electronegativity or inductive effects are more important than other interactions in determining the n.m.r. parameters of these compounds, or at least that the same effects present in the MeR derivatives concur in determining the δ_{Me} of $MeSnR_3$ compounds. The influence of electronegativity on the J(Sn–C–H) coupling constants is difficult to assess, since these constants are restricted to within a small range and also because correlations of coupling constants with substituent electronegativity involve other quantities.[15] However, in Figure 1b it can be seen that chemical shifts δ_{Me} and $J(^{119}Sn\text{–}C\text{–}H)$ in $MeSnR_3$ are roughly proportional. The J(Sn–C–H) coupling constants are highest in the case of 2- and 3-furyl groups, where an oxygen atom is present in the hetero-ring and the group electronegativity should therefore be higher. This seems a clear indication that $(d\text{–}p)\pi$ interactions, if any, have no perceptible influence on long range tin–proton coupling constants of these compounds.

The polarity effects, as expressed by Taft's σ^* constants and checked for other tin [16] and lead [17] derivatives, cannot be examined here since these constants are not known for most of the groups considered.

Previously,[13] we tried to analyse the importance of $(d\text{–}p)\pi$ interactions in alkylhalogenostannanes by examining their spectra in dimethyl sulphoxide (DMSO), complexation of these compounds with the solvent being a well known phenomenon.[18] When dissolved in DMSO, compounds (1) show only small changes both for the δ_{Me} and for J(Sn–C–H), as can be seen from the data reported in Table 1. The coupling constants J(Sn–C–H) are all a little higher in DMSO than in $CDCl_3$, the quantities in the two solvents being proportional. The values relative to the halogeno-substituted compounds are not included in this proportionality. Stannanes with four tin-carbon bonds are reluctant to give co-ordinate complexes,[18] and their coupling constants might be thought to depend on solvent polarity. Further studies on the effects of solvent polarity on long range coupling constants are necessary, and we are now gathering data on this subject.

In order to check whether the findings observed for the tin derivatives regarding $(d\text{–}p)\pi$ interactions may also be extended to other elements with non-zero spin moments and different electronic configuration, some mercury derivatives (2) were examined. The ^1H n.m.r. parameters of these compounds are listed in Table 2. Again, it can be seen from the plot of Figure 2a that the δ_{Me} and J(Hg–C–H) coupling constants for these compounds are linearly correlated, provided that R is not a halogen atom. The linear correlation between $J(^{199}Hg\text{–}C\text{–}H)$ and $J(^{119}Sn\text{–}C\text{–}H)$ reported in Figure 2b for compounds (1) and (2) is also in agreement with the results discussed above; the different behaviour when R is an halogen atom can be explained by the strong $(d\text{–}p)\pi$ interactions present in halogenated compounds.

Further insight into this subject is afforded by the ^1H n.m.r. parameters of some *para*-substituted tetra-aryl compounds (3). The results are shown in Table 3. The chemical shifts of the protons attached to the ring are found at lower field than in benzene itself (δ = 7·23 p.p.m.) and this could apparently indicate that a certain amount of charge might be transferred from the aromatic ring to the tin atom through $(d\text{–}p)\pi$ interactions.[10] If

TABLE 3

Chemical shifts and long range coupling constants J(Sn–H) for $(p\text{-}XC_6H_4)_4Sn$ in $CDCl_3$. *ortho*-Position refers to tin substituents

Compound	δ_o/ p.p.m.	δ_m/ p.p.m.	$J_{o\text{–}m}$/ Hz	$J(^{119}Sn\text{–}H_o)$/ Hz	$J(Sn\text{–}H_m)$/ Hz [d]
(3a) [a]	7·50	6·93	8·6	45·8	8·5
(3b) [b]	7·51	7·17	8·1	47·1	9·9
(3c)	7·60	7·35	7·5	47·2	[c]
(3d)	7·52	7·52	7·8	47·7	[c]

[a] δ_{Me} = 3·78 p.p.m. [b] δ_{Me} = 2·38 p.p.m.; J(Sn–Me) = 3·98 Hz. [c] Not observed owing to the complexity of the spectrum. [d] Coupling constants relative to the two isotopes are indistinguishable.

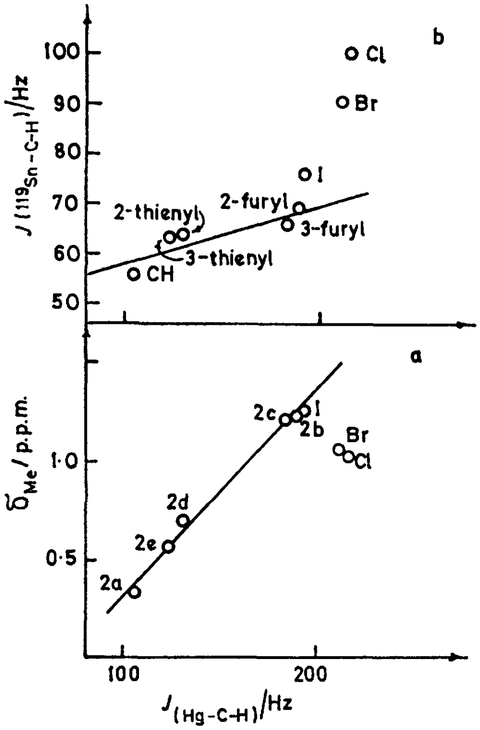

FIGURE 2 Correlation a, of δ_{Me} of compounds (2) and b, of $J(^{119}Sn\text{–}C\text{–}H)$ of compounds (1) against $J(^{199}Hg\text{–}C\text{–}H)$ of compounds (2)

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[15] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 1959, **31**, 1471; N. Dreeskamp and E. Sackmann, *Z. Physik.*, 1962, **34**, 273; L. Lunazzi and F. Taddei, *Boll. sci. Fac. Chim. ind. Bologna*, 1965, **23**, 359.

[16] S. Boué, M. Gielen, and J. Nasielski, *Bull. Soc. chim. belges*, 1967, **76**, 559.

[17] G. Singh, *J. Organometallic Chem.*, 1968, **11**, 133.

[18] C. J. Peddle and G. Redl, *J. Amer. Chem. Soc.*, 1970, **92**, 365, and references therein.

the additivity rule of substituent effects [19] is applied when analysing the chemical shifts, however, it is found that tin and the substituents analysed here behave like groups with very weak conjugative effects, as shown by the comparison below between experimental chemical shifts and those calculated by applying additivity rules of ring protons (the parameters of tin $S_{\mathrm{Sn},o} = -0{\cdot}37$; $S_{\mathrm{Sn},m} = -0{\cdot}12$ were derived from the chemical shifts of *para*-deuteriotetraphenyltin and that of benzene, the other substituent parameters being taken from the literature [19]). The strong deshielding effect both in the *ortho*-positions due to the tin atom and in vinylic and heterocyclic compounds can be attributed perhaps to other effects, such as anisotropy or field effects.[10] The almost constant value for *J*(Sn–C–H) of *ortho*-protons, which was insensitive to the presence of *para*-substituents, should indicate that conjugative interactions between tin and the substituents through the phenyl ring are small, or at least that they do not have a definite effect on these coupling constants.

TABLE 4

	δ_o		δ_m	
X	Calc.	Exper.	Calc.	Exper.
Cl	−0·31	−0·29	−0·19	−0.29
Me	−0·25	−0·27	+0·32	+0·30
OMe	−0·23	−0·28	+0·05	+0·06

In any event, it seems that the presence of small perturbing (*d*–*p*)π interactions cannot be definitely ruled out on the basis of proton chemical shifts, while their effect on long range metal–proton coupling constants might be of only a second order of magnitude. In systems containing solely metal–carbon bonds these interactions should be very small, and probably have no influence on the corresponding σ bonds, thus leaving long-range coupling constants almost unaffected.

EXPERIMENTAL

Spectra.—^{1}H N.m.r. spectra were recorded on a JEOL JNM-C-60HL spectrometer operating at 60 MHz in the internal lock mode. Tetramethylsilane was added as internal standard and locking signal.

Compounds.—Tetramethyltin, methyltriphenyltin, dimethylmercury (2a), and methylmercury iodide were commercial compounds obtained from Alfa Inorganics and employed without further purification. Methyltrivinyltin was prepared by reacting equimolecular amounts of trivinyltin chloride, prepared according to Seyferth and Stone,[20] and methylmagnesium bromide. After hydrolysis with dilute hydrochloric acid the ether layer was dried and evaporated. The oily residue was distilled under reduced pressure, b.p. 48—50 °C at 23 mmHg (Found: C, 48·65; H, 4·8. $C_7H_{12}Sn$ requires C, 48·15; H, 4·8%).

Methyltri-2-thienyltin.—Methyltin trichloride was slowly added at room temperature to an ethereal solution of 2-thienyl-lithium.[12] The oily residue obtained after evaporation of the solvent was distilled, b.p. 147—149 °C at 23 mmHg, n_D^{20} 1·5650 (Found: C, 41·15; H, 3·1. $C_{13}H_{12}SSn$ requires C, 40·65; H, 3·15%).

Methyltri-3-thienyltin.—Methyltin trichloride was slowly added at room temperature to an ethereal solution of 3-thienyl-lithium.[12] The solid obtained after evaporation of the solvent was crystallized from n-pentane, m.p. 98—100 °C (Found: C, 40·4; H, 3·2%).

Tri-2-furylmethyltin.—Methyltin trichloride was slowly added to an ethereal solution of 2-furyl-lithium at −20°.[12] The solid residue obtained after evaporation of the solvent was crystallized from n-pentane, m.p. 76—78 °C (Found: C, 45·65; H, 3·65. $C_{13}H_{12}OSn$ requires C, 46·4; H, 3·55%).

Tri-3-furylmethyltin.—Methyltin trichloride was slowly added to an ethereal solution of 3-furyl-lithium [12] at −70 °C. After evaporation of the solvent the solid residue was crystallized from n-pentane, m.p. 54—56 °C (Found: C, 46·55; H, 3·65%).

2-Furylmethylmercury.—Methylmercury chloride was added to an ethereal solution of 2-furyl-lithium. After evaporation of the solvent the solid residue was crystallized from n-hexane, m.p. 56—58° (Found: C, 20·9; H, 2·2. C_5H_6HgO requires C, 21·25; H, 2·1%).

3-Furylmethylmercury.—To a suspension in ether of methylmercury iodide an equimolecular amount of 3-furylmercury chloride [21] dissolved in tetrahydrofuran was slowly added under vigorous stirring. After hydrolysis with cold water the ethereal layer was separated, and after evaporation of the solvent a solid was obtained which was crystallized from n-hexane, m.p. 94—95° (Found: C, 21·0; H, 2·15%).

Methyl-2-thienylmercury.—The compound was obtained by reacting methylmercury chloride with an equimolecular amount of 2-thienyl-lithium in ether. After evaporation of the solvent the oily residue was treated with n-hexane and a solid material was obtained, m.p. 33—35° (Found: C, 20·05; H, 2·05. C_5H_6HgS requires C, 20·1; H, 2·0%).

Methyl-3-thienylmercury.—The compound was obtained by reacting equimolecular amounts of 3-thienyl-lithium and methylmercury chloride in ether at −70°. The oily residue obtained after evaporation of the solvent was recrystallized from n-hexane, m.p. 150—152° (Found: C, 20·1; H, 2·05%).

Tetrakis-(*p*-methoxyphenyl)tin, tetrakis-(*p*-tolyl)tin, tetrakis-(*p*-deuteriophenyl)tin, and tetrakis-(*p*-chlorophenyl)tin were prepared by reacting the corresponding Grignard reagents obtained from *p*-bromoanisole, *p*-bromotoluene, *p*-bromodeuteriobenzene, and *p*-bromochlorobenzene with tin tetrachloride. The m.p.s of the compounds are 130° (lit.,[22] 134·8°); 233—235° (lit.,[23] 232—234°); 223—225°; and 198—199° (lit.,[24] 197—199°), respectively.

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