Heteronuclear Magnetic Double Resonance Studies of ^{119}Sn Chemical Shifts in Ethyltin Derivatives

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Tin chemical shifts in 32 ethyltin compounds dissolved in inert solvents have been determined by ^{1}H–{^{119}Sn} double resonance experiments. High-field shifts are found when an unsaturated group is attached to tin and this indicates that π-bonding involving the tin 5*d*-orbitals is important. It may be possible to account for the chemical shifts of the halogenated derivatives without invoking π-bonding between tin and the halogen.

IN this paper we present ^{119}Sn chemical shift data for 32 ethyltin compounds and four related derivatives determined by ^{1}H–{^{119}Sn} double resonance experiments.[1] This technique offers substantial advantages in sensitivity and precision over the conventional single resonance method, although the latter advantage is reduced when the tin spectrum is complicated, as in most of our compounds.

Previous workers have used both double and single resonance methods to study tin shielding in miscellaneous methyl and butyl tin compounds, but relatively little systematic work has been done.[2-7]

Although tin has three isotopes of spin ½ attention is usually confined to ^{119}Sn since this is the most abundant (8·7%) and has the highest sensitivity to n.m.r. detection. The primary isotope effect [8] (*i.e.* relative differences in tin shielding in compounds containing ^{119}Sn, ^{117}Sn, and ^{115}Sn) can be expected to be very small and certainly negligible in the present context. Recently $^{117/119}$Sn primary isotope effects of several p.p.m. have been reported in some organotin compounds.[9] However, these have been claimed to be greatest in molecules in which the tin spectrum is either very complex (*e.g.* Et_4Sn) or very broad (*e.g.* Me_2SnCl_2) so that it is difficult to measure the tin chemical shift accurately. We have been unable to reproduce these results, and it certainly appears that the tin chemical shifts quoted here are essentially independent of the particular isotope involved.

EXPERIMENTAL

The compounds studied were prepared as described in Delmas' dissertation,[10] or by standard methods. They were examined under the conditions noted in the Table at 24° on a Jeol spectrometer operating at 60 MHz. R.f. energy at the ^{119}Sn resonant frequency (22·37 MHz) was supplied by a Schlumberger FS30 frequency synthesiser *via* a tuned amplifier to an extra coil mounted in the probe. The r.f. oscillator of the spectrometer was controlled by the frequency synthesiser, and the overall instrumental precision was better than ±0·1 Hz at the tin resonant frequency. Those samples which were neat or dissolved in $CDCl_3$ or CCl_4 also contained a small amount of TMS as a reference. Most spectra were recorded in the field sweep mode and the tin resonant frequencies (Ξ values) [1] quoted in the Table have been corrected to a polarizing field strength in which TMS would give a proton resonance at exactly 100 MHz. The chemical shift (δ) values are downfield of Me_4Sn which is taken [2] as having a Ξ value of 37 290 665 Hz.

RESULTS

In most cases the ^{119}Sn resonant frequency was determined by observing a satellite of the ethyl–methyl resonance and finding the position which gave maximum perturbation. Even when the main ethyl proton resonance displayed strong second order perturbation owing to a small CH_3–CH_2 proton chemical shift difference, the satellites were normally first order and observation of the central component of the methyl satellite triplet gave the centre of the tin resonance pattern. In many cases the tin spectrum contained so many lines that these were not individually resolved and the precision of the measurements was then relatively low. In $EtSnCl_3$ [33] and $EtSnBr_3$ [34] the tin spectrum is quite simple and when a particular component of the methyl triplet satellite is examined only four tin frequencies, separated by $^{3}J(^{119}\text{Sn} \cdots \text{H}) =$ *ca.* 230 Hz should be found. However, these lines were all very broad, and we attribute this to the effect of the $^{35/37}$Cl or $^{79/81}$Br nuclear quadrupole

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

[3] P. G. Harrison, S. E. Ulrich, and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1971, **93**, 5398.

[4] E. V. Van der Berghe and G. P. Van der Kelen, *J. Organometallic Chem.*, 1971, **26**, 207.

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

[6] B. K. Hunter and L. W. Reeves, *Canad. J. Chem.*, 1968, **46**, 1399.

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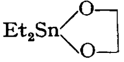
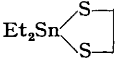
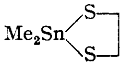
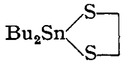
[8] H. Batiz-Hernandez and R. A. Bernheim, *Progr. N.M.R. Spectroscopy*, 1968, **3**, 63.

[9] A. Tupčiauskas, N. M. Sergeyev, and Yu. A. Ustynyuk, *Mol. Phys.*, 1971, **21**, 179.

[10] M. Delmas, *Doctoral dissertation*, Marseille, 1971.

^{119}Sn Chemical shifts in ethyltin derivatives

No.	Compound	Ξ (^{119}Sn) in Hz [a]	δ (^{119}Sn) in p.p.m. [b]	Notes
1	Et_4Sn	37 290 720 ± 20	+1·4	20% in CCl_4 [c]
2	Et_3SnMe	37 290 980 ± 20	+9	20% in CCl_4
3	Et_3SnPh	37 289 380 ± 20	−34	25% in CCl_4
4	Et_3SnBz	37 287 830 ± 50	−6	Sat [d] in CCl_4 [d]
5	Et_3SnVy	37 289 100 ± 40	−42	50% in CCl_4 [e]
6	Et_3SnC_2H	37 288 730 ± 30	−52	30% in CCl_4
7	Et_3SnCl	37 296 430 ± 20	+155	30% in CCl_4
8	Et_3SnBr	37 296 180 ± 20	+148	Neat
9	Et_2SnMe_2	37 290 920 ± 40	+7	20% in CCl_4
10	$Et_2SnBu^t_2$	37 289 940 ± 20	−19	30% in CCl_4
11	Et_2SnPh_2	37 288 220 ± 40	−66	50% in CH_2Cl_2
12	Et_2SnTol_2	37 288 320 ± 20	−63	30% in CCl_4 [f]
13	Et_2SnBz_2	37 290 170 ± 30	−13	40% in C_6H_6 [d]
14	Et_2SnVy_2	37 287 630 ± 40	−81	20% in CCl_4 [e]
15	$Et_2Sn(C_2H)_2$	37 285 400 ± 30	−141	30% in CCl_4
16	Et_2SnCl_2	37 295 160 ± 50	+121	30% in CCl_4 + CH_2Cl_2
17	Et_2SnBr	37 294 230 ± 20	+96	20% in CCl_4
18	Et_2SnI_2	37 288 700 ± 40	+53	15% in CCl_4
19	$Et_2Sn(NMe_2)_2$	37 288 150 ± 50	−67	20% in CCl_4
20	$Et_2Sn(NEt_2)_2$	37 291 430 ± 40	+21	Neat [f, g]
21	$Et_2Sn(OMe)_2$	37 283 920 ± 40	−181	Neat [h]
22	$Et_2Sn(OBu^t)_2$	37 289 500 ± 50	−31	Neat
23		37 284 050 ± 50	−177	25% in $CDCl_3$
24	$Et_2Sn(SMe)_2$	37 295 910 ± 30	+140	20% in CCl_4
25		37 298 110 ± 40	+199	20% in CH_2Cl_2 + $CDCl_3$
26		37 297 880 ± 30	+194	10% in $CDCl_3$
27		37 297 850 ± 30	+193	25% in $CDCl_3$
28	Et_2Sn (oxinate)$_2$	37 280 830 ± 100	−264	25% in CH_2Cl_2
29	$EtSnMe_3$	37 290 760 ± 20	+3	30% in C_6H_6
30	$EtSnPh_3$	37 287 020 ± 20	−98	30% in CCl_4
31	$EtSnBz_3$	37 289 810 ± 20	−23	40% in CH_2Cl_2 [d]
32	$EtSnVy_3$	37 286 040 ± 50	−124	50% in CCl_4 [e]
33	$EtSnCl_3$	37 290 880 ± 20	+6	30% in CCl_4
34	$EtSnBr_3$	37 285 417 ± 10	−141	50% in CCl_4
35	$SnPh_4$		−120	[j]
36	$Sn(C_2H)_4$	37 280 260 ± 30	−279	20% in Et_2O

Tin resonant frequency at a field strength appropriate to a TMS proton resonance of exactly 100 MHz. The fairly large errors arise from the complexity of the tin spectrum. [b] Relative to $(CH_3)_4Sn$ in CH_2Cl_2. A positive δ-value indicates a shift to low field. [c] VPC pure sample. [d] Bz = Benzyl. [e] Vy = Vinyl. [f] Tol = Tolyl; all three isomers had identical chemical shifts within experimental error. [g] Unaffected by dilution (× 8) with benzene. [h] Shifted 16 p.p.m. to low field on dilution to 10% in benzene. [i] Measured at 50° owing to inadequate solubility at room temperature. [j] Estimate—see text.

moments as previously suggested [2] for similar methyl compounds.

It is known that donor solvents can greatly affect tin shielding [7] so solvents have been used which should not interact specifically with the tin compounds. The diamagnetic anisotropy of benzene will not give shifts of more than 1 p.p.m. Effects due to dispersion forces associated with the use of $CDCl_3$, CCl_4, and CH_2Cl_2 will be small because the tin atom is protected from close approach of these molecules by its attached organic groups. Dilution studies performed on selected compounds showed that solvent effects were negligible except in $Et_2Sn(OMe)_2$ [21] where dilution with C_6H_6 shifted the ^{119}Sn resonance *ca.* 16 p.p.m. to lower field at 10% concentration. The limited solubility of [23] precluded a similar study with this compound. The stability of the acetylene derivative $Sn(C_2H)_4$ [36] is low, and the compound was examined in the presence of decomposition products. However, a re-examination of the same sample two months later, when the amount of these was much greater, showed that the ^{119}Sn chemical shift was unaffected.

The ^{119}Sn chemical shift quoted for $SnPh_4$ [35] is an estimate based on the results for several mixed alkyl phenyl tin derivatives since the compound was too insoluble for an experimental value to be obtained.

DISCUSSION

It might be expected that the tin shielding in ethyl derivatives would parallel that found for the corresponding methyl compounds, and the results for the series $Et_{4-n}SnX_n$ (X = Cl or Br, n = 0—4) show that this is so. The characteristic dip in a plot of δ(^{119}Sn) *vs.* n (Figure) with a minimum near $n = 2$ is also given by the analogous methyl compounds and has been attributed to $(p \longrightarrow d)$ π-bonding between the halogen and tin. It is generally accepted that the paramagnetic term dominates the shielding of the heavier nuclei and this depends upon the electron imbalance in the valence p and d orbitals of the atom in question.[11,12] Normally an increase in effective electronegativity of a particular group attached

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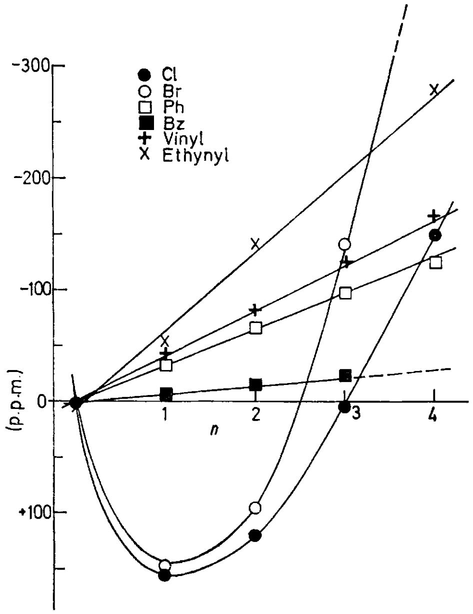
[11] A. Saika and C. P. Slichter, *J. Chem. Phys.*, 1954, **22**, 26.

[12] H. S. Gutowsky and C. Juan, *J. Chem. Phys.*, 1962, **37**, 2198.

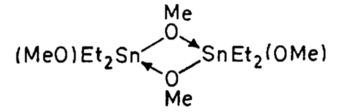
to the tin atom would be expected to increase the imbalance in the *p*-orbitals and so give a shift to lower field, but any use of the tin *d*-orbitals to form π-bonds would tend to offset this effect. If the overall number of electronegative substituents is increased (*i.e.* as *n* increases in the aforementioned series) the effective electronegativity of the tin atom itself will also increase and so the *p*-electron imbalance in each bond may decrease and the tin nucleus may experience increased shielding. It may then be possible to explain the tin chemical shifts in the series $Et_{4-n}SnX_n$ without invoking Sn–X π-bonding. For the compounds $SnCl_xBr_yI_{4-x-y}$ there is a correlation between the tin chemical shift and the effective charge on the tin atom which has been calculated [13,14] by Marrot using an iterative procedure and the electronegativities Sn = 1·80, Cl = 3·0, Br = 2·80, and I = 2·50. There is also a good correlation between the tin chemical shift and the sum of the four charge differences Sn–X in a particular molecule calculated on the same basis. In this case too it appears to be unnecessary to invoke variations in π-bonding to account for the main features of the pattern of the tin chemical shifts.



^{119}Sn Chemical shifts in p.p.m. to low field of $(CH_3)_4Sn$ in $Et_{4-n}SnX_n$

In these molecules, of course, the difference between the charges on the tin atom and all its neighbours is always relatively large, which is not so for the species $R_{4-n}SnX_n$. The importance of the electronegativity of the attached groups in the case of the ethyl derivatives is well brought out by the three compounds Et_2SnX_2 (X = Cl, Br, or I) [16—18].

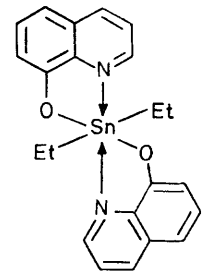
An increase in the co-ordination number of tin from four to five or six is usually accompanied by a substantial increase in the tin shielding, and this has been used to study intermolecular association of tin carboxylates and alkoxides.[15,16] Thus the high field ^{119}Sn chemical shift of $Et_2Sn(OMe)_2$ [21] which decreases on dilution with an inert solvent can be attributed to the dimer (I) or polymers, in which tin is five- or six-co-ordinate. In $Et_2Sn(OBu^t)_2$ [22] the bulk of the t-butoxide groups presumably hinders such association and so the tin is less shielded, whereas in the glycol derivative there is less steric hindrance and a high field shift is observed.



(I)

The low donor power of sulphur towards tin is evident from the low field shifts of the thiol derivatives which are apparently monomeric. It is difficult to assess the effects of ring strain upon tin shielding and so it is not possible to say whether the somewhat higher field shift of $Et_2Sn(SMe)_2$ [24] is due to a small degree of association.

The difference between the chemical shifts of $Et_2Sn(NMe_2)_2$ [19] and $Et_2Sn(NEt_2)_2$ [20] is surprising, and may be due to association in the former giving the relatively high field shift. The chemical shift of [20] agrees reasonably well with that found (+41 p.p.m.) for $Me_2Sn(NEt_2)_2$ earlier,[2] and it may be that the bulkier *N*-ethyl groups hinder association. The very high field chemical shift of [28] is fully consistent with a six-co-ordinate monomeric octahedral structure (II) involving co-ordination by nitrogen. The chemical shifts of mixed alkyl tin derivatives do not appear to be systematic. For example, while substitution of ethyl for methyl in R_4Sn decreases the tin shielding by *ca.* 3 p.p.m. per ethyl group in [29], [9], and [2], the chemical shift of Et_4Sn [1] is only +1 p.p.m. This value differs from one of those quoted (—7 p.p.m.) in the literature but has been obtained from a number of different samples and is thought to be correct. It also agrees with that given in ref 3. Calculations of ^{31}P chemical shifts have shown that these should be least sensitive to changes in the interbond angles at phosphorus when the electronegativity difference between phosphorus and its neighbours is small.[17] If tin shielding behaves similarly it should be possible to



(II)

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[13] J. Marrot, personal communication.

[14] F. Gallais, D. Voigt, and J-F. Labarre, *J. Chim. phys.*, 1965, **62**, 761.

[15] A. G. Davies, L. Smith, P. Smith, and W. McFarlane, *J. Organometallic Chem.*, 1971, **29**, 245.

[16] A. C. Chapman, A. G. Davies, P. G. Harrison, and W. McFarlane, *J. Chem. Soc.* (*C*), 1970, 821.

[17] J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, 1966, **45**, 2926.

attribute the failure of tin chemical shifts to depend additively upon alkyl group substituent parameters to the greater electronegativity difference between Sn and R, and to the small range of variation of the inductive effect for different alkyl groups.

By contrast to the foregoing, the series of compounds:

$Et_{4-n}SnR_n$ (R = $-C_6H_5$, $-CH_2C_6H_5$, $-CH{=}CH_2$, $-C{\equiv}CH$)

have tin chemical shifts which can be predicted by equations (1)—(4),

$$\delta(^{119}Sn)[Ph] = 1{\cdot}5 - 32{\cdot}5\,n \qquad (1)$$

$$\delta(^{119}Sn)[Bz] = 1{\cdot}5 - 7{\cdot}5\,n \qquad (2)$$

$$\delta(^{119}Sn)[Vinyl] = 1{\cdot}5 - 41{\cdot}5\,n \qquad (3)$$

$$\delta(^{119}Sn)[Ethynyl] = 4{\cdot}0 - 68{\cdot}5\,n \qquad (4)$$

The gradients of these four straight lines shown in the Figure are proportional to the corresponding Taft σ^* values for these groups, but are of opposite sign to what would be expected on the basis of an inductive mechanism leading to electron withdrawal by groups with a large σ^* value. For example, the groups $-CHCl_2$ and $-CCl_3$ have σ^* values of 1·94 and 2·65 and lead to ^{119}Sn chemical shifts of +33 and +85 p.p.m. in $Me_3SnCHCl_2$ and Me_3SnCCl_3 respectively.[2] However, these two groups cannot participate in π-bonding with the tin atom, whereas this is possible with the phenyl, benzyl (*via* a hyperconjugative mechanism), vinyl, and ethynyl groups. Other evidence that the phenyl group can form π-bonds to Group IV elements is summarized elsewhere.[18] This will involve the tin *d*-orbitals and so should lead to an increase in the tin shielding. The large shifts to high field which occur when tin increases its co-ordination number to more than four show that involvement of the tin *d*-orbitals can outweigh the downfield shift due to the greater *p*-electron imbalance associated with more electronegative ligands. If the π-bonding is reinforced synergically by the σ-bond interaction it should be greatest for groups with the largest Taft σ^* values which should therefore give the shifts at highest field, as is observed.

We therefore conclude that $p\pi$–$d\pi$ interactions are important in compounds in which tin is attached to one or more unsaturated groups, but that it may be possible to account for tin chemical shifts in tin and organotin halides without invoking π-bonding between tin and the halogen atoms. This latter conclusion is to some extent supported by studies of ^{119}Sn shielding in $Me_nSn(SCH_3)_{4-n}$ compounds.[4]

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[2/554 *Received, 9th March,* 1972]

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[18] J. M. Angelelli, J. C. Maire, and Y. Vignollet, *Annales Fac. Sci. Marseille*, 1970, **43***A*, 47.