Nuclear Magnetic Double Resonance Studies of Organotin Selenides

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^{1}H, ^{13}C, ^{77}Se, and ^{119}Sn chemical shifts, and the signs and magnitudes of coupling constants involving these nuclei, have been measured by nuclear magnetic double resonance techniques in the series $Me_{4-n}(SeR)_n$ (n = 1—4, R = Me or Ph). The results are interpreted mainly on the basis of inductive electron withdrawal from the tin atom by the electronegative RSe– groups.

THE increased sensitivity of modern n.m.r. spectrometers and the use of Fourier transform and multiple resonance techniques has led to a substantial increase in the amount of data available on coupling constants and chemical shifts for the heavier nuclei.[1,2] In many cases the chemical shifts have not been satisfactorily explained, even on a semi-empirical basis, and one of the problems is that investigations have often been confined to the study of only one or two parameters in a series of compounds, so that trends in electron densities and other factors which might affect the nuclear shielding have to be estimated intuitively rather than assessed more precisely. In this paper we present chemical shifts and coupling constants for two series of organotin selenides $Me_{4-n}Sn(SeR)_n$ (R = Me, Ph; n = 1—4) in which all of the atoms have an isotope of nuclear spin $\frac{1}{2}$ of at least

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[1] D. G. Gillies and D. Shaw, *Ann. Reports N.M.R. Spectroscopy*, 1972, **5**, 557.

[2] W. McFarlane, *Ann. Reports N.M.R. Spectroscopy*, 1972, **5**, 353.

moderate natural abundance. It was thus possible to study nuclear shielding at up to six different sites in each molecule and to measure seven different coupling constants. The $^{1}H-\{X\}$ double resonance technique was used on account of the high sensitivity of the observed nucleus, and because it is very convenient when several different nuclear species are to be studied. Typically it was possible to determine two $^{13}C-H$, two $^{77}Se-H$, two $^{119}Sn-H$, and the $^{119}Sn-^{77}Se$ coupling constants and the ^{1}H, ^{13}C, ^{77}Se, and ^{119}Sn chemical shifts in less than 1 h of instrument time for each compound.

Previously tin magnetic shielding has been studied in miscellaneous collections of compounds [3-8] and also in series of methyltin sulphides [9] and organotin carboxylates.[10] Some of this work has been interpreted in terms of $d\pi-p\pi$ bonding between tin and electronegative donor atoms (*e.g.*, chlorine or sulphur) and it would be very useful if tin shielding could be used to measure the extent of this type of interaction. Less is known about selenium chemical shifts but correlations with the electronegativity of attached groups have been established.[11]

TABLE 1

Analytical and physical data for organotin selenides

Compound	B.p. [t/°C (p/mmHg)]	Colour [a]	Calculated (%) C	H	Se	Found (%) C	H	Se
$Me_3SnSeMe$ [c]	82—84 (2)	Colourless	18·6	4·69	30·6	18·9	4·60	30·8
$Me_2Sn(SeMe)_2$	90—92 (1)	Colourless	14·3	3·57	46·9	14·3	3·57	47·9
$MeSn(SeMe)_3$	94—96 (0·5)	Very pale yellow	11·6	2·91	57·0	11·8	2·91	56·7
$Sn(SeMe)_4$	Oil [b]	Pale yellow	9·71	2·45	63·9	9·74	2·41	63·9
$Me_3SnSePh$ [d]	91—94 (0·5)	Very pale yellow	33·8	4·41	24·7	34·2	4·34	24·6
$Me_2Sn(SePh)_2$ [e]	150—152 (0·02)	Pale yellow	36·5	3·50	34·3	36·9	3·44	34·4
$MeSn(SePh)_3$	212—214 (0·01)	Yellow	37·9	3·01	39·4	37·7	2·98	39·3
$Ph_3SnSeMe$	m.p. 84—85	White	51·4	4·09	17·8	51·5	3·98	17·9

[a] Colour of freshly distilled material; even brief exposure to air leads to darkening. [b] Decomposed before boiling, at 0·01 mmHg. [c] Lit., b.p. 26 °C at 0·8 mmHg; E. W. Abel, B. C. Crosse, and G. V. Hutson, *J. Chem. Soc.* (*A*), 1967, 2014. [d] Lit., b.p. 67—69 °C at 0·001 mmHg; E. W. Abel, D. A. Armitage, and D. B. Brady, *J. Organometallic Chem.*, 1966, **5**, 130. [e] M.p., 34—37 °C; lit., m.p. 32—33 °C, ref. as for note *c*.

EXPERIMENTAL

The compounds $Me_{4-n}Sn(SeR)_n$ (R = Me, Ph; n = 1—4) were made on a scale of *ca.* 10 mmol by mixing cooled ether solutions of the correct molar proportions of $Me_{4-n}SnCl_n$, MeSeH, or PhSeH, and triethylamine, stirring at room temperature for 1 h and filtering off the precipitated triethylammonium chloride. Ether was then removed under vacuum and the product was isolated by distillation, except in the case of $Sn(SeMe)_4$ which was purified by differential extraction with carbon tetrachloride–light petroleum (b.p. 40—60 °C). $Ph_3SnSeMe$ was made by allowing equimolar amounts of hexaphenylditin and dimethyldiselenide to react for several days in dichloromethane. A sample of $Me_3SnSeMe$ which was prepared similarly from hexamethylditin had the same physical properties and n.m.r. parameters as one prepared by the amine route. Analytical data and selected physical properties are in Table 1. The compounds appeared to be stable for an indefinite time when stored in sealed vessels but slowly decomposed on exposure to the atmosphere.

The ^{1}H n.m.r. spectra were recorded at 60 MHz and 24 °C with, for most measurements, neat samples containing small amounts of dichloromethane and Me_4Si for field-frequency locking and reference purposes. Solutions (*ca.* 5%) in carbon tetrachloride were used for the proton chemical shifts. The isotopes ^{13}C, ^{77}Se, and ^{119}Sn were present in natural abundance (1·1, 7·5, and 8·7% respectively) and the double resonance equipment has been described.[11] The ^{1}H n.m.r. data for $Me_3SnSeMe$ agree with those reported.[12]

RESULTS

In pure samples of the compounds ^{119}Sn satellites of the *Se*-methyl groups were always clearly visible, but in the presence of small amounts of the $Me_{4-n}SnCl_n$ or $Ph_{4-n}SnCl_n$ precursors these disappeared. We attribute this to rapid equilibria of the type (1) involving nucleophilic attack on

$$Me_3SnCl + Me_3{}^{119}SnSeMe \rightleftharpoons Me_3{}^{119}SnCl + Me_3SnSeMe \quad (1)$$

the tin atom and the participation of intermediate five-co-ordinate species. This will lead to loss of the coupling between ^{119}Sn and the protons of the *Se*-methyl groups, but retention of that between ^{119}Sn and the *Sn*-methyl groups, as was observed. Similar effects have been noticed in organotin sulphides.[12]

In general the ^{13}C, ^{77}Se, and ^{119}Sn chemical shifts were determined by observing the appropriate satellites in the proton spectrum and performing tickling experiments.[13] However $^{3}J(^{77}Se-H)$ was too small for selenium satellites

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

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

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

[6] A. Tupčiauskas, N. M. Sergeyev, and Yu. A. Ustynyuk, *Org. Magnetic Resonance*, 1971, **3**, 655.

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

[8] W. McFarlane, J. C. Maire, and M. Delmas, *J.C.S. Dalton*, 1972, 1862.

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

[10] W. McFarlane and R. J. Wood, *J. Organometallic Chem.*, 1972, **40**, C 17.

[11] W. McFarlane and R. J. Wood, *J.C.S. Dalton*, 1972, 1397.

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

[13] R. Freeman and W. A. Anderson, *J. Chem. Phys.*, 1962, **37**, 2053.

of the *Sn*-methyl groups to be resolved, but an increase of *ca.* 5% in the height of the central *Sn*-methyl resonance was *obtained* when the selenium resonance was irradiated. This indicated that 1 Hz > $|{}^3J({}^{77}\text{Se-H})|$ > 0·4 Hz and permitted the determination of selenium chemical shifts in compounds without an *Se*-methyl group. The sharpening of the tin satellites which was attained by irradiation at the selenium resonant frequency was used to obtain accurate values of tin–selenium coupling constants in molecules containing both ^{77}Se and ^{117}Sn or ^{119}Sn. These experiments are illustrated in Figure 1 for $Me_2Sn(SePh)_2$. Values of coupling constants involving ^{117}Sn are omitted from Table 2 because in all cases it was found that $J({}^{119}\text{Sn-X})/J({}^{117}\text{Sn-X}) = \gamma({}^{119}\text{Sn})/\gamma({}^{117}\text{Sn})$ to within experimental error. Similarly, no significant ^{119}Sn/^{117}Sn isotope effect upon the tin shielding was noted and the chemical shifts are given for ^{119}Sn only.

The signs of the coupling constants are relative to $^2J({}^{119}\text{Sn} \cdots \text{H}) > 0$, and allowance was made for the negative magnetogyric ratios of ^{119}Sn and ^{117}Sn in their derivation. Molecules containing both ^{13}C and a magnetic tin isotope were of such low natural abundance that in most cases it was not possible to determine tin–carbon coupling constants. However, it is known that in general variations in $^nJ({}^{119}\text{Sn-}{}^{13}\text{C})$ for a given organic group on tin are paralleled by those in $^{(n+1)}J({}^{119}\text{Sn} \cdots \text{H})$ so the absence of these data is not too serious.[14]

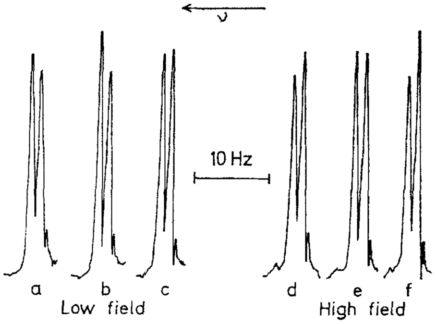

FIGURE 1 ^{117}Sn and ^{119}Sn satellites of the methyl-proton resonance of $Me_2Sn(SePh)_2$. a and d, normal single resonance spectra; b, with simultaneous irradiation of the ^{119}Sn satellite at low field in the ^{77}Se spectrum; $^3J({}^{77}\text{Se} \cdots \text{H})$ is collapsed selectively to give a small increase in the height of the ^{119}Sn proton satellite; c, with irradiation of the ^{117}Sn satellite at low field in the ^{77}Se spectrum; e, with irradiation of the ^{117}Sn satellite at high field in the ^{77}Se spectrum; f, with irradiation of the ^{119}Sn satellite at high field in the ^{77}Se spectrum

The results are in Table 2 and in calculating the chemical shifts the following values were used for the resonant frequencies of the reference compounds. Me_4Si: $\Xi({}^{13}\text{C})$ = 25,146,005 Hz; Me_2Se: $\Xi({}^{77}\text{Se})$ = 19,071,523 Hz; and Me_4Sn: $\Xi({}^{119}\text{Sn})$ = 37,290,665 Hz. Figures 2 and 3 summarize the variations with *n* of the coupling constants and chemical shifts respectively in the species $Me_{4-n}(SnMe)_n$.

TABLE 2

N.m.r. parameters of organotin selenides

	$Me_3SnSeMe$	$Me_2Sn(SeMe)_2$	$MeSn(SeMe)_3$	$Sn(SeMe)_4$	$Me_3SnSePh$	$Me_2Sn(SePh)_2$	$MeSn(SePh)_3$	$Ph_3SnSeMe$
$^1J({}^{119}\text{Sn-}{}^{77}\text{Se})$/Hz	1015 ± 10	1190 ± 10	1340 ± 10	1520 ± 10	980 ± 10	1190 ± 10	1400 ± 15	1210 ± 15
$^2J({}^{119}\text{Sn} \cdots \text{H})$/Hz	55·5	57·6	59·6	—	55·5	57·0	57·4	—
$^3J({}^{119}\text{Sn} \cdots \text{H})$/Hz	−31·1	−37·7	−46·2	−55·2	—	—	—	−35·1
$^2J({}^{77}\text{Se} \cdots \text{H})$/Hz	9·8	10·2	10·6	10·6	—	—	—	10·3
$^1J({}^{13}\text{C-H})$(Sn)/Hz	129·4	132·6	135·6	—	130·8	133·9	136·8	—
$^1J({}^{13}\text{C-H})$(Se)/Hz	141·5	142·4	143·5	144·2	—	—	—	143·0
δ(H)(Sn)/p.p.m.	0·46	0·80	1·12	—	0·40	0·55	0·45	7·4—8·1
δ(H)(Se)/p.p.m.	1·81	1·97	2·08	2·18	7·0—7·5	7·0—7·5	7·0—7·5	1·83
δ(^{13}C)(Sn)/p.p.m.	−5·2	−1·3	+3·0	—	−3·7	+0·05	+8·4	—
δ(^{13}C)(Se)/p.p.m.	−3·2	−0·7	+1·7	+3·5	—	—	—	−1·7
δ(^{119}Sn)/p.p.m.	+45·6	+57·1	+14·8	−80·5	+55·0	+54·1	−16·5	−69
δ(^{77}Se)/p.p.m.	−276·7	−237·0	−183·9	−127·3	+ 11·3	+65·5	+124·0	−320

Coupling constants are ± 0·2 Hz unless otherwise stated. Chemical shifts are in p.p.m. to low field of the reference (Me_4Si for ^{1}H and ^{13}C, Me_4Sn for ^{119}Sn, and Me_2Se for ^{77}Se) and are ± 0·02 p.p.m. for ^{1}H and ± 0·1 p.p.m. for the other nuclei.

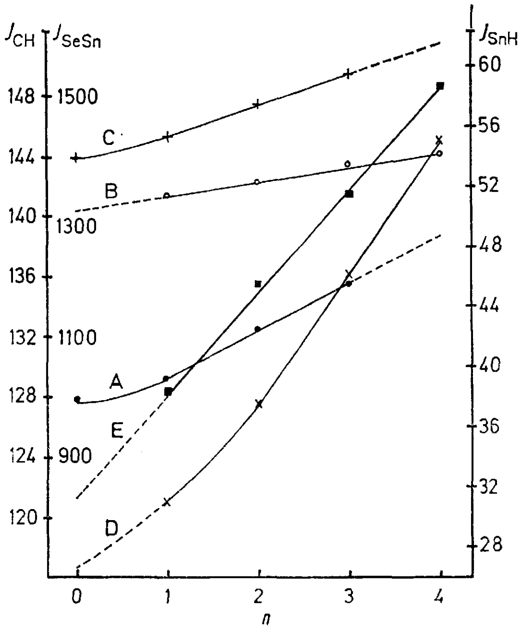

FIGURE 2 Coupling constants as a function of *n* in the series $Me_{4-n}Sn\ (SeMe)_n$. A, $^1J({}^{13}\text{C-H})$(Sn); B, $^1J({}^{13}\text{C-H})$(Se); C, $^2J({}^{119}\text{Sn} \cdots \text{H})$; D, $-\,{}^3J({}^{119}\text{Sn} \cdots \text{H})$; E, $^1J({}^{119}\text{Sn-}{}^{77}\text{Se})$

DISCUSSION

Spin coupling constants between the nuclei of directly bound elements generally increase as the effective nuclear charge of either element increases and as the *s*-character of the orbitals used to form the bond increases. There may be exceptions to this in the case of elements with electron lone pairs such as fluorine and

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[14] W. McFarlane, *J. Chem. Soc.*, 1967, 528.

selenium when the pattern of variation is more complex.[15-19] An important consequence of this behaviour is that $^1J(^{13}C\text{-}H)$ in a methyl group can be used to provide a good estimate of electron density on the atom to which the methyl group is attached, since the coupling constant will increase as this electron density decreases.[16] This result applies irrespective of which mechanism is considered to dominate the changes in $^1J(^{13}C\text{-}H)$, namely, the increased effective nuclear charge of carbon, or the diversion of *s*-character into the hybrid orbitals used by carbon to form the C–H bond. In our compounds replacement of *Sn*-methyl groups by selenium should increase the effective electronegativity of the tin atom and so lead to an increase in $^1J(^{13}C\text{-}H)$ in the remaining *Sn*-methyl groups, as observed. A similar effect should be found for $^1J(^{13}C\text{-}H)$ in the *Se*-methyl groups although it should be smaller since the relevant methyl group is one bond further from the point of variation. In fact the observed ratio of the slopes of the plots of $^1J(^{13}C\text{-}H)$ (Sn) and $^1J(^{13}C\text{-}H)$ (Se) against *n* is 3·5 and this is in agreement with the generally accepted view that in carbon compounds inductive effects fall by a factor of *ca.* 3 for each additional intervening single bond.[20]

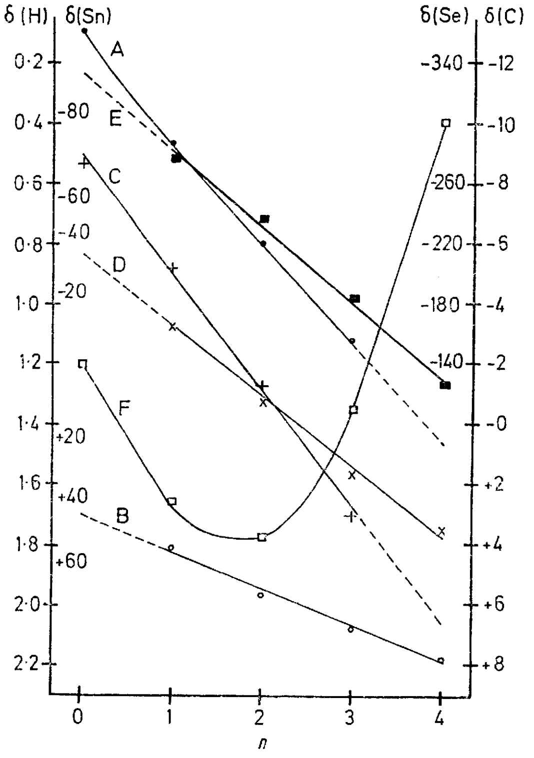

FIGURE 3 Chemical shifts/p.p.m. to low field of the reference as a function of *n* in the series $Me_{4-n}Sn(SeMe)_n$. A, $\delta(^1H)(Sn)$; B, $\delta(^1H)(Se)$; C, $\delta(^{13}C)(Sn)$; D, $\delta(^{13}C)(Se)$; E, $\delta(^{77}Se)$; F, $\delta(^{119}Sn)$

The positive sign for $^1J(^{77}Se\text{-}^{119}Sn)$ corresponds to a negative sign for $^1K(SeSn)$ since $\gamma(^{119}Sn) < 0$, and this is in agreement with negative signs previously found for $^1K(SeC)$ [21] and $^1K(SeSi)$.[22] According to the molecular orbital treatment of Pople and Santry these negative signs will arise because the 4*s*-orbitals of selenium are of relatively low energy and so the *s*-overlap integral between selenium and carbon, silicon, or tin is small. The mutual polarizability term which appears when the mean excitation energy approximation is not made is then negative. It should therefore be found that the *magnitude* of the coupling constant should increase as the other groups attached to the tin atom become more electron-withdrawing: that is, as the effective nuclear charge of the tin atom increases and/or the *s*-character of the tin hybrid orbital used for the Sn–Se bond becomes greater. Our results confirm that this is so, and each successive replacement of an *Sn*-methyl group by the more electronegative SeMe leads to an increase in $^1J(^{77}Se\text{-}^{119}Sn)$ of *ca.* 170 Hz. Similarly, replacement of all three *Sn*-methyl groups in $Me_3SnSeMe$ by phenyl groups increases the coupling constant. Replacement of *Sn*-methyl by SePh increases $^1J(^{77}Se\text{-}^{119}Sn)$ by *ca.* 220 Hz per methyl group replaced; this is reasonable in view of the greater electron-withdrawing ability to be expected for SePh than for SeMe. The sizes of all these increases are about what would be expected by comparison with the accompanying changes in $^1J(^{13}C\text{-}H)$ of the *Sn*-methyl groups.

It is difficult to predict the effect upon $^1J(^{77}Se\text{-}^{119}Sn)$ of altering the group attached to selenium because not only will the effective nuclear charge of selenium and the *s*-character of the selenium hybrid used for the Se–Sn bond change, but also the Se–Sn *s*-overlap integral may alter substantially and these changes could either augment or oppose one another. In fact, replacement of *Se*-methyl by phenyl *decreases* $^1J(^{77}Se\text{-}^{119}Sn)$ in $Me_3SnSeMe$, *increases* it in $MeSn(SeMe)_3$, and leaves it unchanged in $Me_2Sn(SeMe)_2$. However, in all these three cases $^1J(^{13}C\text{-}H)$ in the *Sn*-methyl groups is *increased* when *Se*-methyl is replaced by phenyl so it appears that there is greater electron-withdrawal by the phenyl group, and hence the observed variation of $^1J(^{77}Se\text{-}^{119}Sn)$ probably arises largely from a change in the *s*-overlap integral for the Se–Sn bond. In addition it may be necessary to consider π-bonding interactions between selenium and the phenyl groups.

The two- and three-bond $^{119}Sn\text{-}H$ couplings will depend upon geminal and dihedral angles as well as electronic distribution but in the compounds studied the bulk of the substituents is too small to make any marked conformational preferences likely.

If $^3J(^{119}Sn \cdots H)$ is dominated by the Fermi contact interaction it should be increased by any increase in the

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

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

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

[18] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[19] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1969, **51**, 2790.

[20] J. Clark and D. D. Perrin, *Quart. Rev.*, 1964, **18**, 295.

[21] W. McFarlane, *Mol. Phys.*, 1967, **12**, 243.

[22] H. Esler and H. Dreeskamp, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 619.

effective charge of tin and/or of the *s*-character of the Sn–Se bond. The behaviour of this coupling constant should therefore parallel that of $^1J(^{77}Se–Sn)$ and in fact these two coupling constants are increased by *ca.* 77% and 50% respectively in going from $Me_3SnSeMe$ to $Sn(SeMe)_4$. This behaviour is qualitatively what would be expected, but a plot of one coupling constant against the other does not pass through the origin. The intercept of −17·3 Hz on the $^3J(^{119}Sn \cdots H)$ axis may represent a contribution other than the Fermi contact interaction to this coupling; however, there is some curvature of the plot for small *n* which in itself shows that the effective nuclear charge of tin and the *s*-character of the tin hybrid orbitals used to form the Sn–Se bond cannot be the only variables affecting *both* coupling constants.

Replacement of *Sn*-methyl by SeMe in a compound $Me_{4-n}Sn(SeMe)_n$ will increase the *s*-character of all the other three tin hybrid orbitals. However, this change will be relatively smallest for the Sn–C bonds (for which the *s*-character is already high) and consequently the effects upon $^2J(^{119}Sn \cdots H)$ should be less than upon coupling constants which involve the Sn–Se bonds. This (together with the change in effective nuclear charge of the tin atom) may account for the change in $^2J(^{119}Sn \cdots H)$ of only *ca.* 10% which accompanies replacement of three *Sn*-methyl groups by SeMe, but it seems likely that there is also a contribution to this coupling constant from another mechanism. This has been suggested previously from a comparison of $^1J(^{119}Sn–^{13}C)$ and $^2J(^{119}Sn \cdots H)$ in methyltin halides.[14] Unfortunately the signal-to-noise ratio attainable in the present study did not permit measurement of the tin–carbon coupling constants to confirm this.

The trend shown by $^2J(^{77}Se \cdots H)$ is consistent with electron-withdrawal from tin as the number of SeMe groups increases, but the extent of the change is too small for detailed discussion to be profitable.

Trends in chemical shifts of nuclei other than the proton can often be discussed satisfactorily in terms of differing degrees of electron-withdrawal by substituents provided that the point of variation is more than one bond removed from the atom containing the nucleus in question.[23] For protons the effects of substituent magnetic and electric anisotropies and of van der Waals forces can be of greater importance. Generally it is found that increasing electron-withdrawal gives a decrease in magnetic shielding (*i.e.*, on our sign convention δ increases) and this is so irrespective of whether the diamagnetic or the paramagnetic contribution to the shielding is dominant. The ^1H and ^{13}C chemical shifts in methyl groups in the series $Me_{4-n}Sn(SeMe)_n$ are in agreement with the foregoing, and the greater sensitivity of the shieldings in the *Sn*-methyl groups to changes in *n* is to be expected since these groups are closer to the point of variation than are the *Se*-methyl groups. Indeed, the proton chemical shifts suggest that the change in electron density as *n* varies at an *Sn*-methyl group is *ca.* 3 times that at an *Se*-methyl group, a conclusion similar to that drawn from consideration of the $^{13}C–H$ coupling constants.

The ratios $\Delta\delta(^{13}C) : \Delta\delta(^1H)$ (where $\Delta\delta$ is the change in chemical shift as *n* varies) for the *Sn*- and *Se*-methyl groups are 12·4 and 18·6 respectively. Comparison of these values with the same ratios in substituted methanes CH_3X and in a series of methyl carboxylates[24] suggests that the polarizability of the tin atom is greater than that of selenium in these molecules. The *Sn*-methyl proton chemical shifts in the derivatives of phenylselenol will be affected by the diamagnetic anisotropy of the aromatic rings and cannot be discussed usefully.

Studies of a wide range of organoselenium compounds have shown that the selenium nucleus becomes less shielded as the electron-withdrawing ability of the attached groups increases.[11] This has been attributed to a change in the paramagnetic term resulting from an altered electron imbalance in the bonds to selenium.[25] The results for the organotin selenides are consistent with this view.

There is a decrease in the selenium shielding of *ca.* 50 p.p.m. with each replacement of *Sn*-methyl by SeMe, and somewhat more for replacement by SePh. This difference may be due to the greater electron-withdrawing ability of SePh than of SeMe (*cf.* the effect on the ^{13}C shielding in the *Sn*-methyl groups), but it is also possible that the magnetic shielding of selenium bound to phenyl is more sensitive to changes in electronic environment. On the basis of the above arguments it is difficult to account for the high-field ^{77}Se chemical shifts of $Ph_3SnSeMe$ compared with $Me_3SnSeMe$ since the Ph_3Sn moiety would be expected to be more electron-withdrawing than Me_3Sn–. However, this might not be so if there were π-overlap between the phenyl rings and the tin atom, and also possibly between tin and selenium.

In the two series $Me_{4-n}Sn(SeR)_n$ (R = Me, Ph) the various coupling constants and the ^1H, ^{13}C, and ^{77}Se chemical shifts can therefore be accounted for satisfactorily on the basis of systematic electron-withdrawal from the tin atom as *n* increases, but the ^{119}Sn chemical shifts are not so readily explained. Curve F of Figure 3 has the same appearance as plots of $\delta(^{119}Sn)$ against *n* in many series $R_{4-n}SnX_n$ where X is an electronegative atom such as halogen, nitrogen, oxygen, or sulphur.[4–9] It has not, however, previously been as clearly established that the electron density on tin does in fact vary in the expected manner. Three interpretations have been offered for this behaviour: (*a*) changes in the size of the diamagnetic contribution to the shielding;[26] (*b*) π-bonding involving filled *p*-orbitals on X and vacant *d*-orbitals on tin;[4–9] and (*c*) dispersion forces.[5] Our results do not permit us to discriminate among these

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[23] P. R. Wells, 'Determination of Organic Structures by Physical Methods,' ed. F. C. Nachod and J. J. Zuckerman, Academic Press, New York, 1971, **4**, 233.

[24] W. McFarlane, *J. Chem. Soc.* (*B*), 1969, 28.

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

[26] J. Mason, *J. Chem. Soc.* (*A*), 1971, 1038.

explanations, but it should be pointed out that dominance by the paramagnetic term will lead to a dependance of δ(^{119}Sn) upon the *p*- and *d*-electron imbalance in the bonds to the tin atom.[25] This in turn will depend upon the effective electronegativity difference between the tin atom itself and its substituents. As the number of electronegative groups attached to tin increases the effective electronegativity of tin will also increase and the electronegativity difference associated with a particular bond will decrease. This in turn will reduce the electronic imbalance and may lead to increased shielding of the tin atom. It may be therefore that in many cases the importance of effects (*a*), (*b*), and (*c*) is less than has been suggested.

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