Heteroaryltin Compounds. Preparation and Characterisation of some 3-Furyltin Halides. Tin-119 Nuclear Magnetic Resonance and Mössbauer Studies of a Series of Heteroaryltin Compounds

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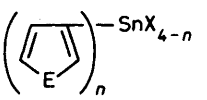
A series of 3-furyltin halides of the types SnR_nX_{4-n} (R = 3-furyl; n = 2 or 3; X = Cl or Br) have been prepared and characterised by chemical and spectroscopic techniques. Mössbauer data for triphenylphosphine oxide adducts of the tris(3-furyl)tin halides are consistent with five-co-ordinate trigonal-bipyramidal structures bearing equatorial heteroaryl groups. The bis(3-furyl)tin dihalides have been characterised by complex formation with 2,2′-bipyridyl and Mössbauer studies suggest a six-co-ordinate *cis*-octahedral environment for tin. The 3-furyltin halides have been found to be considerably more stable than their 2-furyl and 2-thienyl analogues. Continued attempts to characterise these less stable compounds by complex formation have met with some success. ^{119}Sn N.m.r. data are presented for the above series of heteroaryltin compounds and also for a range of tetrakis(heteroaryl)tin systems. The ^{119}Sn n.m.r. and Mössbauer data are discussed in terms of the possible electronic effects of the heteroaryl groups.

The chemistry of tin compounds of the types SnR_3X and SnR_2X_2 (X = halogen) bearing a heteroaryl group directly linked to tin *via* a carbon of the heterocyclic ring has been little studied. In view of the variety of heterocyclic ring systems, and the established biological activity [1] of organotin compounds of the type SnR_3X, together with the recent interest in complexes of diorganotin dihalides as antitumour agents,[2] we have commenced an exploration of this area. In a recent paper,[3] we described the preparation of a range of 3-thienyltin halides, $Sn(3\text{-}C_4H_3E)_nX_{4-n}$ (1; n = 2 or 3; E = S; X = Cl, Br, or I), and some complexes of these with donor ligands. We also reported preliminary details of the preparation of the related 2-thienyl- and 2-furyl-tin halides, $Sn(2\text{-}C_4H_3E)_nX_{4-n}$ (2; n = 2 or 3; E = O or S; X = Cl, Br, or I), and their characterisation by Mössbauer spectroscopy. However, the latter compounds proved to be much less stable than the 3-thienyltin halides, and attempts to characterise them chemically were frustrated by their ready decomposition in solution.

We now describe the preparation and characterisation of 3-furyltin systems (1; n = 2 or 3; E = O; X = Cl or Br), together with further studies of the chemistry of the unstable 2-furyl- and 2-thienyl-tin halides (2; n = 2 or 3; E = O or S; X = Cl or Br), including attempts to prepare stable complexes of these compounds. We also present ^{119}Sn n.m.r. data for a range of heteroarylorganotin compounds and draw attention to the contrasting effects of so-called 'π excessive' heterocyclic substituents on ^{119}Sn chemical shifts and ^{119}Sn Mössbauer isomer shifts in a given series of compounds.

Results and Discussion

The tris(3-furyl)tin halides (1; n = 3; E = O; X = Cl or Br) were obtained by the redistribution reactions of tetrakis(3-furyl)tin with the appropriate tin(IV) halide (3 : 1 mol ratio) at 100—110 °C for 1—2 h. The compounds were purified by recrystallisation and isolated as air-stable, analytically pure solids, although the bromide gradually darkened on standing. The Mössbauer spectra of the solids (recorded at 80 K) show quadrupole-split doublets, without significant line broadening, having parameters similar to those of the related 3-thienyl- and phenyl-tin halides (Table 1). The magnitudes of the quadrupole splitting [and of the Herber ratio Δ/δ (ref. 4)] are indicative of four-co-ordination at tin, and hence it would seem that these compounds are not associated to any significant extent in the solid state, *e.g.* as a result of intermolecular co-ordinate interactions between the oxygen of the ring system and the tin atom of another molecule. Neither has any evidence of this type of interaction been found in an *X*-ray structural study of tris(3-thienyl)tin bromide.[5]



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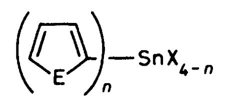

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Comparison of the Mössbauer data for these compounds with those of the 3-thienyl- and phenyl-tin halides reveals that both the isomer shift and the quadrupole splitting are lower than those of the 3-thienyl and phenyl analogues. The reduction in isomer shift implies a reduction in *s*-electron density at tin, and the order of apparent electron-withdrawing ability of the organic substituents is phenyl < 3-thienyl < 3-furyl, consistent with the increasing electron affinity of the heteroatom.

Both $Sn(3\text{-}C_4H_3O)_3Cl$ and $Sn(3\text{-}C_4H_3O)_3Br$ readily form insoluble 1 : 1 complexes on treatment with equimolar amounts of triphenylphosphine oxide in toluene solution, as do the 3-thienyl analogues. Co-ordination of the phosphoryl oxygen is indicated by a significant reduction in the P=O i.r. stretching frequency compared with that of the free ligand, as observed for the related complex of $SnPh_3Cl$.[6] The Mössbauer parameters of the adducts are very similar to those reported for the Ph_3PO complexes of $SnPh_3Cl$ and $SnPh_3Br$, for which trigonal-bipyramidal structures involving equatorial phenyl groups have been assumed on the basis of partial quadrupole splitting (p.q.s.) calculations.[7,8]

The bis(3-furyl)tin dihalides (1; n = 2; E = O; X = Cl or Br) have also been obtained by redistribution reactions of

Table 1. ^{119}Sn Mössbauer and n.m.r. data for 3-furyltin halides and related compounds

Compound	Isomer shift [a] δ/mm s^{-1}	Quadrupole splitting [b] Δ/mm s^{-1}	δ/p.p.m. [c]	N.m.r. solvent [d] [concentration w/v (%)]
$Sn(3-C_4H_3O)_3Cl$	1.12	2.07	−40.1	$CDCl_3$ (5)
$Sn(3-C_4H_3O)_3Br$	1.18	2.03	−80.8	$CDCl_3$ (20)
$Sn(3-C_4H_3O)_3Cl\cdot Ph_3PO$	1.09	3.16	−129.0	$CDCl_3$ (5)
$Sn(3-C_4H_3O)_3Br\cdot Ph_3PO$	1.12	3.12	−183.8	CD_2Cl_2 (5)
$Sn(3-C_4H_3S)_3Cl$	1.21	2.29 [e]	−70.3	$CDCl_3$ (10)
$Sn(3-C_4H_3S)_3Br$	1.25	2.08 [e]	−100.6	$CDCl_3$ (5)
$Sn(3-C_4H_3S)_3Cl\cdot Ph_3PO$	1.18	3.08 [e]	−147.6	$CDCl_3$ (5)
$Sn(3-C_4H_3S)_3Br\cdot Ph_3PO$	1.21	3.03 [e]	−167.0	CD_2Cl_2 (5)
			−209.2	CD_2Cl_2 (5) [f]
$SnPh_3Cl$	1.37	2.45 [g]	−48.0 [h]	CD_2Cl_2 (5)
$SnPh_3Br$	1.37	2.46 [e]		
$Sn(3-C_4H_3O)_2Cl_2$	1.14	2.55	−8.8	$CDCl_3$ (80)
$Sn(3-C_4H_3O)_2Br_2$	1.23	2.19	−102.7	$CDCl_3$ (50)
$Sn(3-C_4H_3O)_2Cl_2\cdot$bipy	0.76	2.02	—	Insoluble
$Sn(3-C_4H_3O)_2Br_2\cdot$bipy	0.83	2.13	—	Insoluble
$Sn(3-C_4H_3S)_2Cl_2$	1.23	2.55	−38.6	$CDCl_3$ (80)
$Sn(3-C_4H_3S)_2Br_2$	1.30	2.30	−113.7	$CDCl_3$ (30)
$Sn(3-C_4H_3S)_2Cl_2\cdot$bipy	0.86	2.00	—	Insoluble
$Sn(3-C_4H_3S)_2Br_2\cdot$bipy	1.22	3.26	—	Insoluble
$SnPh_2Cl_2$	1.34	2.89 [i]	−32.0 [h]	CD_2Cl_2
$SnPh_2Br_2$	1.43	2.54 [j]		
$Sn(3-C_4H_3O)Cl_3$	—	—	−51.0	$CDCl_3$ [k]
$Sn(3-C_4H_3O)Br_3$	—	—	−268.5	$CDCl_3$ [k]
$Sn(3-C_4H_3S)Br_3$	—	—	−264.8	$CDCl_3$ [k]

[a] Relative to $BaSnO_3$; ±0.02 mm s^{-1}. [b] ±0.02 mm s^{-1}. [c] Relative to $SnMe_4$; ±0.5 p.p.m. [d] Ambient temperature except where stated otherwise. [e] Ref. 3. [f] At 0 °C. [g] Ref. 4. [h] A. G. Davies, P. G. Harrison, J. D. Kennedy, T. N. Mitchell, R. J. Puddephatt, and W. McFarlane, *J. Chem. Soc. C*, 1969, 1136. [i] H. A. Stockler and H. Sano, *Trans. Faraday Soc.*, 1968, **64**, 577. [j] R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 1970, **4**, 65. [k] This compound was present as a redistribution product of the SnR_2X_2 species; see text.

equimolar amounts of tetrakis(3-furyl)tin with tin(IV) halide. Both are liquids, which we have been unable to crystallise. The Mössbauer spectra of the frozen liquids (Table 1) reveal the expected quadrupole-split doublets, and, as for the related bis(3-thienyl)tin dihalides, indicate four-co-ordinate tin in unassociated, discrete molecules. The Mössbauer isomer shifts reveal similar trends to those obtained for the triorganotin halides with respect to the electron-withdrawing properties of the substituents at tin. Both $Sn(3-C_4H_3O)_2Cl_2$ and $Sn(3-C_4H_3O)_2Br_2$ were characterised by the formation of 1 : 1 complexes with 2,2′-bipyridyl (bipy) on treatment of the dihalide with an equimolar amount of the ligand in toluene solution. Mössbauer data for these complexes are consistent with *cis*-octahedral structures, by analogy with data for related diorganotin dihalide complexes.[9] It is of interest to note that in the case of the corresponding bipy complexes of the bis(3-thienyl)tin dihalides, the dibromo-complex appears to have a distorted *trans*-octahedral structure.[3] The preparation of $Sn(3-C_4H_3O)_2I_2$ was also attempted by the redistribution reaction, and attempts were made to characterise it by complex formation with bipy. However, analytical data and Mössbauer spectroscopy indicated that the product of the reaction was probably a mixture of the desired di-iodide and $Sn(3-C_4H_3O)I_3$. This, together with the limited stability of $Sn(3-C_4H_3O)_3Br$, may be some indication that the 3-furyltin halides do not enjoy the same degree of stability as their 3-thienyl analogues.

Thus, it is clear that the 3-heteroaryltin halides are very similar in general properties to the well known phenyltin halides. In spite of the propensity of tin to increase its co-ordination from four to five or six, often *via* intermolecular association, there is in these compounds no evidence of such interactions involving the oxygen or sulphur atoms of the heterocyclic rings. The observed instability of the related 2-heteroaryl derivatives is presumably due to the ease with which they undergo ' protodestannylation' reactions, a reflection of the tendency of furan and thiophen to undergo rapid electrophilic substitution in the 2-position. The increased stability of the 3-heteroaryl derivatives is consistent with this point of view.[10]

We have attempted to characterise representative members of the 2-heteroaryltin halides (2; X = O or S; n = 2 or 3) by complex formation immediately following their preparation by redistribution reactions. Some degree of success has been achieved in characterising the bis(2-heteroaryl)tin dihalides by complex formation with bipy and 1,10-phenanthroline. Mössbauer data for the bipy complexes of $Sn(2-C_4H_3O)_2Br_2$ and $Sn(2-C_4H_3S)_2Cl_2$ are included in Table 2. From the magnitude of the quadrupole splitting parameters, it would appear that the former has a distorted *trans*-octahedral structure, whereas the latter is likely to be *cis* octahedral. However, the quadrupole splitting parameter for $Sn(2-C_4H_3S)_2Cl_2\cdot$bipy is rather low for a *cis*-SnR_2X_4 type of system, and it is possible that this compound has a more complex structure in the solid state.* Indeed, the Mössbauer spectrum exhibits some degree of asymmetry, although the linewidths are consistent with the presence of only one tin site.

The use of Ph_3PO as a ligand for the complexation of the tris(2-heteroaryl)tin halides in toluene solution resulted in the formation of microcrystalline, insoluble complexes. However, although i.r. and Mössbauer data were consistent with expected structures, microanalytical data revealed consistently high carbon figures, and it is likely that these complexes are mixtures of $SnR_3X\cdot Ph_3PO$ and $SnR_2X_2\cdot 2Ph_3PO$, the latter arising from the disproportionation of the initially formed triorganotin halide in solution. Similarly, reactions between

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* It is of interest that the complex *cis*-diphenylbis(8-quinolinolato)-tin(IV) also exhibits a quadrupole splitting of 1.69 mm s^{-1} (R. V. Parish and C. E. Johnson, *J. Chem. Soc. A*, 1971, 1906).

Table 2. ^{119}Sn Mössbauer and n.m.r. data for 2-heteroaryl tin halides and related compounds

Compound	Isomer shift [a] δ/mm s^{-1}	Quadrupole splitting [b] Δ/mm s^{-1}	δ/p.p.m. [c]	N.m.r. solvent [d] [concentration w/v (%)]
$Sn(2-C_4H_3O)_3Cl$	1.14	2.14	−164.0	$CDCl_3$ (20)
$Sn(2-C_4H_3O)_2Cl_2$	1.10	2.09	−110.9	$CDCl_3$ (80)
$Sn(2-C_4H_3O)_3Br$	1.17	2.19	See text	
$Sn(2-C_4H_3O)_2Br_2$	1.17	1.80	−205.0	Neat liquid
$Sn(2-C_4H_3O)Br_3$	—	—	−324.8 [e]	$CDCl_3$
$Sn(2-C_4H_3S)_3Cl$	1.13	1.99	−64.4	$CDCl_3$ (50)
$Sn(2-C_4H_3S)_2Cl_2$	1.14	2.06	−39.3	$CDCl_3$ (80)
$Sn(2-C_4H_3S)Cl_3$	—	—	−77.6 [e]	$CDCl_3$
$Sn(2-C_4H_3S)_3Br$	1.18	1.99	−104.6	$CDCl_3$ (5)
$Sn(2-C_4H_3S)_2Br_2$	1.17	1.80	−134.8	$CDCl_3$ (5)
$Sn(2-C_4H_3O)_2Br_2$·bipy	0.98	2.85	—	Insoluble
$Sn(2-C_4H_3S)_2Cl_2$·bipy	0.75	1.69	—	Insoluble

[a] Relative to $BaSnO_3$; ±0.02 mm s^{-1}. [b] ±0.02 mm s^{-1}. [c] Relative to $SnMe_4$; ±0.5 p.p.m. [d] Ambient temperature. [e] This compound was present as a redistribution product of the SnR_2X_2 species, see text.

Table 3. ^{119}Sn Mössbauer [a] and n.m.r. data for tetraheteroaryltin compounds

Compound	Isomer shift [b] δ/mm s^{-1}	δ/p.p.m. [c]	N.m.r. solvent [d] [concentration w/v (%)]
(*a*) SnR_4			
R = 2-Furyl	1.06	−260.2	$CDCl_3$ (10)
		−266.3	C_5H_5N (10)
		−276.1	dmso (10)
R = Benzo[*b*]fur-2-yl	1.08	−250.3	$CDCl_3$ (1)
R = 3-Furyl	1.09	−156.0	$CDCl_3$ (10)
		−158.3	C_5H_5N (5)
		−161.2	dmso (5 and 10)
R = 2-Thienyl	1.10	−147.0	$CDCl_3$ (7)
		−150.7	C_5H_5N (5)
		−165.3	dmso (3)
R = Benzo[*b*]thien-2-yl	1.12	−144.1	$CDCl_3$ (0.5)
R = 3-Thienyl	1.16	−168.7	$CDCl_3$ (0.5)
R = Ph	1.26	−137.0 [e]	$CDCl_3$ (10)
(*b*) $SnR^1{}_nR^2{}_{4-n}$			
$R^1 = R^2$ = *p*-Tolyl	1.28	−123.3	$CDCl_3$ (3)
R^1 = *p*-Tolyl, R^2 = 3-thienyl, *n* = 2	—	−146.3	$CDCl_3$ (10)
R^1 = *p*-Tolyl, R^2 = 3-thienyl, *n* = 1	—	−157.8	$CDCl_3$ (10)
$R^1 = R^2$ = 3-Thienyl	1.16	−168.7	$CDCl_3$ (0.5)

[a] Δ = 0.00 mm s^{-1} for all compounds. [b] Relative to $BaSnO_3$; ±0.02 mm s^{-1}. [c] Relative to $SnMe_4$; ±0.5 p.p.m. [d] Ambient temperature. [e] Ref. 13.

tris(2-heteroaryl)tin halides and a *p*-tolyl Grignard reagent resulted in the formation of several mixed tetraorganostannanes. Direct evidence of the instability of the tris(2-heteroaryl)tin halides in solution has been obtained from ^{119}Sn n.m.r. studies on solutions of the organotin compounds in deuteriochloroform immediately following their preparation. Thus, for example, a solution of $Sn(2-C_4H_3O)_3Cl$ exhibited a signal at −164 p.p.m., which on standing diminished in intensity, while signals appeared at −260 and −110.9 p.p.m., arising from $Sn(2-C_4H_3O)_4$ and $Sn(2-C_4H_3O)_2Cl_2$, respectively. These signals increased in intensity with time. The corresponding $Sn(2-C_4H_3O)_3Br$ is even less stable, no signal for this compound being observed; the spectrum of a freshly prepared solution (previously characterised in the 'pure' state by Mössbauer spectroscopy) exhibited signals at −260 and −205.0 p.p.m., attributable to $Sn(2-C_4H_3O)_4$ and $Sn(2-C_4H_3O)_2Br_2$ respectively.

These observations provide some insight into the difficulties encountered in trying to characterise the tris(2-heteroaryl)tin halides chemically. Both methods employed required the reactive substrate to be in solution, prior to treatment with either a monodentate ligand, to form a stable complex, or with a Grignard reagent, when attempting to prepare a mixed tetraorganostannane. The expected product of the redistribution reaction between $Sn(2-C_4H_3O)_4$ and tin(IV) bromide (3 : 1 molar ratio) is $Sn(2-C_4H_3O)_3Br$. In the absence of a solvent, a solid product crystallises out and its Mössbauer parameters are consistent with those expected for the desired compound. However, when this product is dissolved in either toluene or chloroform and treated with a solution of a bidentate ligand, an insoluble complex is formed. The analytical data obtained for this compound are consistent with the formation of the diorganotin dihalide adduct.

A similar pattern is observed in the solution behaviour of the tris(2-thienyl)tin halides, although the rate of disproportionation is much reduced compared to the 2-furyl analogues. As expected, the 3-heteroaryltin halides are much more stable in solution, and do not appear to undergo disproportionation. ^{119}Sn N.m.r. chemical shifts for the heteroaryltin halides and their derivatives are given in Tables 1 and 2. Related data for a series of tetraheteroarylstannanes are presented in Table 3. In the course of this work, a number of mono-organotin tri-

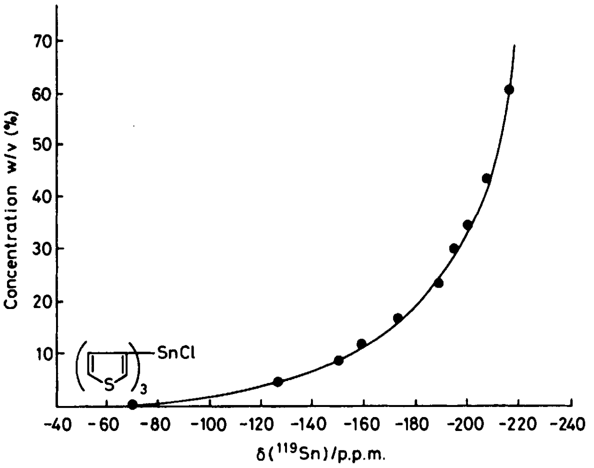

Figure 1. Concentration dependence of ^{119}Sn n.m.r. chemical shift of the $\mathrm{Sn(3\text{-}C_4H_3S)_3Cl{\cdot}Ph_3PO}$ adduct in $\mathrm{CDCl_3}$, at 33 °C

halides were observed, *either* as products of disproportionation of bis(2-heteroaryl)tin halides, *or* as minor impurities present in the more stable systems. The ^{119}Sn n.m.r. signals for these compounds (Tables 1 and 2) exhibit considerable broadening due to quadrupolar interactions between the halogens and ^{119}Sn, and occur at low frequency, consistent with the established, apparent increase in shielding of the tin nucleus as the number of halogens increases.

^{119}Sn N.m.r. studies of the phosphine oxide adducts of the tris(heteroaryl)tin halides reveal the expected increase in shielding of the tin nucleus on complex formation, as has been observed for related complexes of the phenyltin halides.[11] The ^{119}Sn chemical shifts of these compounds are found to be concentration dependent, and, to some extent, temperature dependent. Figure 1 shows the concentration dependence, at 33 °C, for $\mathrm{Sn(3\text{-}C_4H_3S)_3Cl{\cdot}Ph_3PO}$ in deuteriochloroform. This effect implies a mobile equilibrium in solution between uncomplexed, four-co-ordinate tris(heteroaryl)tin halide and the five-co-ordinate adduct, the observed upfield change in chemical shift being consistent [12,13] with the increase in co-ordination number of the tin atom.

Although the difficulties inherent in the interpretation of trends in ^{119}Sn n.m.r. chemical shift data with changes in substituents are well recognised,[12–14] it is nevertheless of interest to consider the electronic effects of the above range of heteroaryl substituents. Such heterocyclic systems are commonly referred to as 'π excessive' and assumed to be 'electron-rich' systems. However, this view is only valid where the π system of the ring can interact in a conjugative manner with a substituent atom having a vacant orbital, with which $p_\pi \rightarrow p_\pi$ or $p_\pi \rightarrow d_\pi$ interactions can take place. It is possible that such substituents could therefore be involved in $p_\pi \rightarrow d_\pi$ interactions with the tin atom, and this has been held responsible for the increased (diamagnetic) shielding of the tin atom in the series $\mathrm{SnMe_{4-\mathit{n}}(2\text{-}C_4H_3O)_\mathit{n}}$ as the number of 2-furyl substituents increases.[15] We have observed a parallel trend in the series Sn(*p*-tolyl)$_{4-n}$(3-thienyl)$_n$ as the *p*-tolyl groups are replaced by the more 'π excessive' 3-thienyl system (Table 3). Similar increases in shielding of tin are observed in the series $\mathrm{SnEt_{4-\mathit{n}}Z_\mathit{n}}$ (n = 0—4, Z = Ph, vinyl, or $^{-}$C≡CH) when the alkyl groups are replaced by the π systems, again suggesting that π interactions with the tin 5*d* orbitals may be of some importance.[16] It has been pointed out, however, that it is far from clear as to the effect which such π bonding might have upon tin shielding, although it is likely that it would reduce the paramagnetic term,[13] usually considered to be the dominant factor contributing to the nuclear shielding.[14]

The above heteroaryl substituents, due to the presence of the electronegative heteroatom, are also able to function as σ electron-withdrawing systems, and we have noted many instances of this in the chemistry of the main Group 5 elements, notably phosphorus and arsenic.[17] Such electronegativity effects of directly-bonded substituents are known to be complex.[12,13] Not only would such substituents encourage synergic $p_\pi \rightarrow$ Sn d_π back-donation, but intermolecular σ co-ordination involving the tin atom would also be possible. However, the latter would be expected to result in concentration dependent ^{119}Sn n.m.r. data, and this has not been observed in the present study. Any interpretation of the effects of such heteroaryl substituents on ^{119}Sn n.m.r. chemical shifts is therefore fraught with difficulty.

The same is true for the interpretation of ^{119}Sn Mössbauer isomer shifts for these compounds. It is accepted that ^{119}Sn Mössbauer shifts reflect the 5*s* electron density at the tin nucleus, and that a decrease in the isomer shift indicates electron withdrawal from tin. However, occupation of tin 5*d* orbitals as a result of π bonding may also cause a decrease in 5*s* electron density at the nucleus as a result of increased atomic core shielding.

The Mössbauer and ^{119}Sn n.m.r. parameters for a range of tetrakis(heteroaryl)tin compounds are given in Table 3. It is noteworthy that, in general, substituents which result in a lowering of the ^{119}Sn Mössbauer chemical shift (implying σ electron withdrawal and/or π bonding to tin) have the effect of *increasing* the shielding of the tin in the n.m.r. experiment and moving the resonance to lower frequency (higher field). Tetrakis(2-furyl)tin has a significantly reduced Mössbauer isomer shift compared to $\mathrm{SnPh_4}$ (and the lowest value of δ in the series), and yet has the most shielded tin nucleus in the n.m.r. experiments. The slightly higher degree of nuclear shielding in $\mathrm{Sn(3\text{-}C_4H_3S)_4}$ compared with $\mathrm{Sn(3\text{-}C_4H_3O)_4}$ may point to some degree of synergic π bonding in these compounds. A similar inverse correlation between Mössbauer isomer shifts and ^{119}Sn n.m.r. chemical shifts is also apparent (but to a lesser degree) in the heteroaryltin halides (Tables 1 and 2).

We have sought additional evidence of the electron-withdrawing properties of the above heteroaryl substituents in the tetraheteroarylstannanes. Tetraorganostannanes show extremely weak acceptor properties and do not form solid adducts with donor molecules, with the possible exception of $\mathrm{SnMe_3CF_3}$ which is reported [18] to form a 1 : 1 complex with $\mathrm{P(NMe_2)_3}$. In addition, it is interesting to note that the ^{119}Sn n.m.r. chemical shift of $\mathrm{Sn[C_6H_4(CF_3)\text{-}\mathit{m}]_4}$ in dimethyl sulphoxide (dmso) shows a 10 p.p.m. shift to low frequency (increased shielding) compared to that in deuteriochloroform,[19] whereas a low frequency shift of only 1.6 p.p.m. is found for $\mathrm{SnMe_4}$ in similar solvents.[20] We find that there is a low frequency shift of 16 p.p.m. for $\mathrm{Sn(2\text{-}C_4H_3O)_4}$ when deuteriochloroform is replaced by dmso. Similarly, when pyridine is used as the solvent, there is a 6 p.p.m. shift to low frequency (see Table 3). Using the same solvent systems, comparable upfield shifts have been observed for $\mathrm{Sn(2\text{-}C_4H_3S)_4}$ and, to a lesser extent, for $\mathrm{Sn(3\text{-}C_4H_3O)_4}$ (Table 3). However, it was noted that these shifts appear to exhibit very little concentration dependence over the accessible concentration range. These increases in shielding of the tin nucleus may indicate donor–acceptor interactions involving the tin, which are favoured by the σ electron-withdrawing properties of the 2-furyl and 2-thienyl substituents. In contrast, addition of $\mathrm{Ph_3PO}$ to a solution of $\mathrm{Sn(2\text{-}C_4H_3O)_4}$ in deuteriochloroform causes no shift in the ^{119}Sn signal. However, when $\mathrm{Sn(2\text{-}C_4H_3O)_4}$ and $\mathrm{Ph_3PO}$ are melted together, the Mössbauer

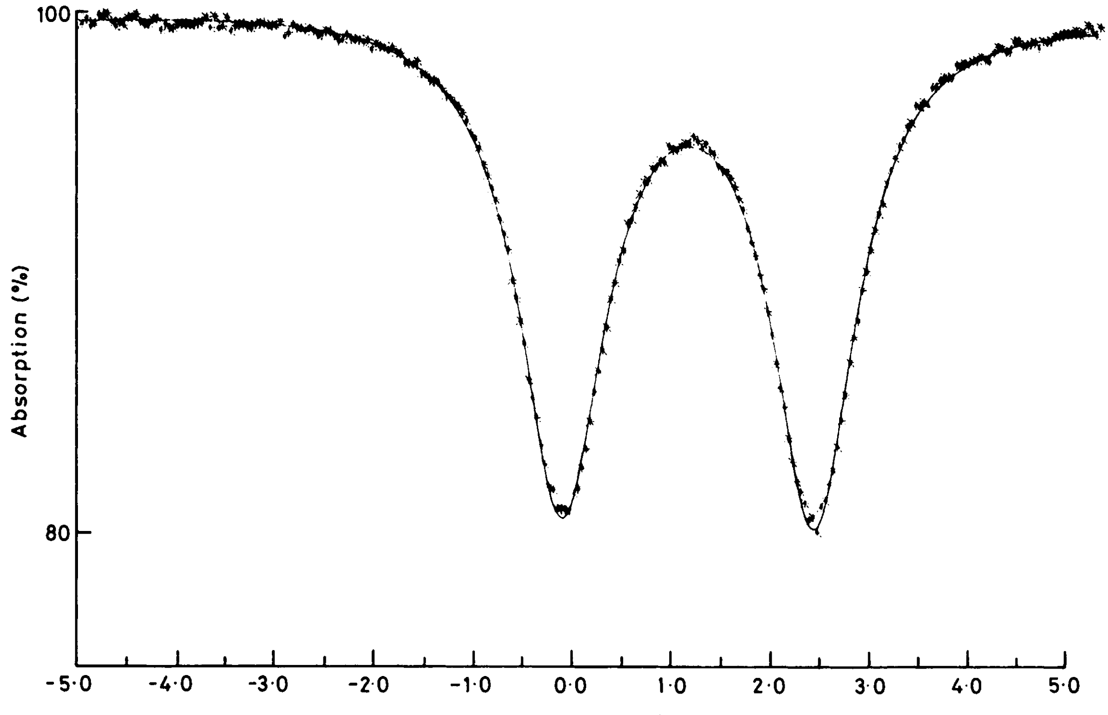

Figure 2. ^{119m}Sn Mössbauer spectrum of Sn(3-$C_4H_3O)_2Cl_2$ at 80 K

spectrum of the solidified melt shows considerable complexity and could possibly be interpreted in terms of an overlapping quadrupole-split doublet and a singlet, the latter corresponding to uncomplexed tetraorganostannane. Thus, there may be some degree of justification in attributing significant electron-withdrawing properties to the 2-heteroaryl groups in these stannanes, but it seems possible that $p_\pi \rightarrow d_\pi$ effects may, in addition, have a role to play in the interaction between such ring systems and tin.

Experimental

Mössbauer Data.—^{119}Sn Mössbauer spectra were obtained using a constant acceleration spectrometer. A 15-mCi $BaSnO_3$ source was used at room temperature, the samples sealed in Perspex discs and cooled to 80 K using a continuous flow nitrogen cryostat with helium exchange gas. The isomer shift and quadrupole splitting parameters were obtained from computer least-squares fits to the spectra using Lorentzian line shapes. A typical Mössbauer spectrum is shown in Figure 2.

^{119}Sn *N.M.R. Measurements.*—^{119}Sn N.m.r. spectra were recorded on a JEOL FX60Q instrument at 33 °C in 10-mm tubes. The nuclear Overhauser effect was suppressed by the use of the gated decoupling technique.[21] Field frequency lock was to external D_2O. Chemical shifts are relative to $SnMe_4$ and are accurate to ±0.5 p.p.m.

All the reactions described were carried out under an inert atmosphere of either nitrogen or argon. The compounds Sn(3-$C_4H_3O)_4$, Sn(2-$C_4H_3O)_4$, Sn(2-$C_4H_3S)_4$, and Sn(3-$C_4H_3S)_4$ were prepared as previously described.[3,22] The preparation of all 3-thienyltin compounds can be found in an earlier paper.[3]

Tris(3-furyl)tin Chloride.—Tetrakis(3-furyl)tin (1.0 g, 2.58 × 10^{-3} mol) and $SnCl_4$ (0.1 cm^3, 8.68 × 10^{-4} mol) were heated together, with stirring, at an oil-bath temperature of 100 °C, for 2 h. The product crystallised on cooling and was purified by recrystallisation from hexane to give white crystals (0.45 g) m.p. 76.5—79 °C (Found: C, 40.55; H, 2.55; Cl, 9.70. $C_{12}H_9ClO_3Sn$ requires C, 40.55; H, 2.55; Cl, 10.0%).

Tris(3-furyl)tin Bromide.—Tetrakis(3-furyl)tin (0.5 g, 1.29 × 10^{-3} mol) and $SnBr_4$ (0.19 g, 4.33 × 10^{-4} mol) were heated together, with stirring, at an oil-bath temperature of 110 °C for 1 h. The product crystallised on cooling and was recrystallised from hexane to yield white crystals (0.28 g) which showed gradual signs of decomposition (darkening) on standing for several days, m.p. 77.5—80 °C (Found: C, 35.7; H, 2.15; Br, 20.65. $C_{12}H_9BrO_3Sn$ requires C, 36.05; H, 2.25; Br, 20.0%).

Triphenylphosphine Oxide Complexes of Tris(3-furyl)tin Halides.—A toluene solution of the tris(3-furyl)tin halide was treated in the cold, with stirring, with an equimolar amount of Ph_3PO, also dissolved in toluene. The following complexes crystallised out on ice-cooling with the dropwise addition of hexane. (*a*) Sn(3-$C_4H_3O)_3Cl\cdot Ph_3PO$ (yield: 73%), m.p. 118—120 °C (Found: C, 56.95; H, 3.80; Cl, 5.65. $C_{30}H_{24}ClO_4PSn$ requires C, 56.85; H, 3.80; Cl, 5.60%). I.r. (Nujol mull): 1 158 cm^{-1} (co-ordinated P=O). (*b*) Sn(3-$C_4H_3O)_3Br\cdot Ph_3PO$ (yield: 80%), m.p. 134—135 °C (Found: C, 53.1; H, 3.50; Br, 11.85; P, 4.75. $C_{30}H_{24}BrO_4PSn$ requires C, 53.15; H, 3.55; Br, 11.8; P, 4.55%). I.r. (Nujol mull): 1 145 cm^{-1} (co-ordinated P=O).

Bis(3-furyl)tin Dichloride-2,2'-Bipyridyl (1/1).—Tetrakis(3-furyl)tin (0.5 g, 1.29 × 10^{-3} mol) and $SnCl_4$ (0.15 cm^3, 1.29 × 10^{-3} mol) were heated together, with stirring, at an oil-bath temperature of 110 °C for 1.5 h. The resulting liquid was dissolved in toluene, filtered, and treated with a toluene solution of 2,2'-bipyridyl (0.4 g, 2.56 × 10^{-3} mol) to give an insoluble complex (0.55 g), m.p. 255 °C (decomp.) (Found: C, 45.1; H, 3.00; N, 5.85. $C_{18}H_{14}Cl_2N_2O_2Sn$ requires C, 45.05; H, 2.95; N, 5.85%).

Bis(3-*furyl*)*tin Dibromide*-2,2′-*Bipyridyl* (1/1).—Tetrakis(3-furyl)tin (0.5 g, 1.29 × 10^{-3} mol) and $SnBr_4$ (0.56 g, 1.28 × 10^{-3} mol) were heated together, with stirring, at an oil-bath temperature of 110 °C for 2 h. The resulting liquid was dissolved in toluene, filtered, and treated with a toluene solution of 2,2′-bipyridyl (0.4 g, 2.56 × 10^{-3} mol) to yield an insoluble white complex (0.81 g), m.p. 230 °C (decomp.) (Found: C, 37.4; H, 2.50; N, 4.90. $C_{18}H_{14}Br_2N_2O_2Sn$ requires C, 38.0; H, 2.50; N, 4.90%).

Bis(2-*thienyl*)*tin Dichloride*-2,2′-*Bipyridyl* (1/1).—Tetrakis-(2-thienyl)tin (1.0 g, 2.22 × 10^{-3} mol) and $SnCl_4$ (0.25 cm³, 2.17 × 10^{-3} mol) were heated together, with stirring, at an oil-bath temperature of 100 °C for 1.5 h. The liquid product was dissolved in toluene and filtered, in a nitrogen atmosphere, into a toluene solution of 2,2′-bipyridyl (0.68 g, 4.35 × 10^{-3} mol) to form a finely-divided insoluble complex, m.p. >240 °C (decomp.) (Found: C, 42.0; H, 2.90; N, 5.25. $C_{18}H_{14}Cl_2N_2S_2Sn$ requires C, 42.2; H, 2.75; N, 5.45%).

Bis(2-*furyl*)*tin Dibromide*-2,2′-*Bipyridyl* (1/1).—(*i*) Tetrakis-(2-furyl)tin (0.5 g, 1.29 × 10^{-3} mol) and $SnBr_4$ (0.56 g, 1.28 × 10^{-3} mol) were heated together, with stirring, for 0.75 h at an oil-bath temperature of 90 °C. The resultant liquid was taken up in toluene and filtered, under nitrogen, into a toluene solution of 2,2′-bipyridyl (0.4 g, 2.56 × 10^{-3} mol) resulting in the immediate formation of a dense white precipitate, m.p. >200 °C (decomp.) (Found: C, 37.1; H, 2.30; N, 4.80. $C_{18}H_{14}Br_2N_2O_2Sn$ requires C, 38.0; H, 2.50; N, 4.90%).

(*ii*) Tetrakis(2-furyl)tin (0.5 g, 1.29 × 10^{-3} mol) and $SnBr_4$ (0.19 g, 4.33 × 10^{-4} mol) were heated together, with stirring, at an oil-bath temperature of 80 °C for 1 h. On cooling, a solid product crystallised out; this material was dissolved in toluene and filtered, under nitrogen, into a toluene solution of 2,2′-bipyridyl (0.13 g, 8.32 × 10^{-4} mol); a finely divided white precipitate was quickly formed, m.p. 236 °C (decomp.) (Found: C, 38.5; H, 2.55; N, 5.05. $C_{18}H_{14}Br_2N_2O_2Sn$ requires C, 38.0; H, 2.50; N, 4.90%).

Tetrakis(*benzo*[b]*thien*-2-*yl*)*tin*.—Butyl-lithium (1.48 mol dm⁻³, 75 cm³, 1.11 × 10^{-1} mol) was added dropwise to benzo[*b*]thiophen (17 g, 1.27 × 10^{-1} mol) in dry diethyl ether (50 cm³) with ice cooling. The reaction mixture was stirred at room temperature for 2 h. $SnCl_4$ (3.0 cm³, 2.60 × 10^{-2} mol, in hexane) was added dropwise with continued stirring, the reaction mixture heated under reflux for a further 2 h, and hydrolysed by pouring into water with vigorous stirring. The solid product was filtered off, alkali-washed (NaOH), and recrystallised from toluene, m.p. 254—257 °C. Yield 9.90 g (59%) (Found: C, 59.6; H, 3.15; S, 18.95. $C_{32}H_{20}S_4Sn$ requires C, 59.0; H, 3.10; S, 19.7%).

Tetrakis(*benzo*[b]*fur*-2-*yl*)*tin*.—Butyl-lithium (1.48 mol dm⁻³, 60 cm³, 8.88 × 10^{-2} mol) was added dropwise to benzo[*b*]furan (12 g, 1.02 × 10^{-1} mol) in diethyl ether (50 cm³) with cooling (ice–salt) and stirred for 3 h. $SnCl_4$ (2.4 cm³, 2.08 × 10^{-2} mol) was added dropwise as a hexane solution and the reaction mixture stirred under reflux for a further 2 h. After cooling, the mixture was hydrolysed, the product filtered off, alkali-washed (NaOH), and recrystallised from toluene, m.p. 231.5—233 °C. Yield 7.85 g (64%) (Found: C, 65.85; H, 3.55. $C_{32}H_{20}O_4Sn$ requires C, 65.45; H, 3.45%).

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