*The chemistry of some heteroaryltin compounds.*

DERBYSHIRE, Diana Jane.

# THE CHEMISTRY OF SOME HETEROARYLTIN COMPOUNDS

by

DIANA JANE DERBYSHIRE

A Thesis submitted to the Council for
National Academic Awards in Partial fulfilment
of the requirements for the Degree of Doctor of Philosophy

| | |
|---|---|
| Sponsoring Establishment: | Department of Chemistry,<br>Sheffield City Polytechnic |
| Collaborating Establishment: | International Tin Research<br>Institute |

June 1986

# The Chemistry of Some Heteroaryltin Compounds

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Diana Jane Derbyshire

The objective of this study was to prepare a series of previously unreported heteroaryl organotin compounds bearing thienyl and furyl substituents, where the heteroaryl group is bound to tin via a heteroaromatic ring carbon atom. In particular, compounds bearing, respectively, two and three heteroaryl groups were of greatest interest, as diorgano- and triorganotin compounds have previously been found to be most significant in terms of their biological applications. The desired compounds have been prepared and subsequently characterised by spectroscopic, chemical and analytical techniques. (Some of the compounds are being evaluated for potential usefulness in the areas of pest control and chemotherapy).

Chapter 1 provides an insight into the present uses of organotin compounds. The electronic properties of the chosen heterocyclic substituents are also reviewed and their possible influence on the properties of the proposed organotin compounds discussed. A survey of the literature relating to heteroaryltin compounds is presented.

Chapter 2 commences with an overview of probable synthetic methods for the desired compounds based, in particular, on the chemistry of related phenyltin compounds. The di- and tri(2-heteroaryl)tin compounds are found to be unstable to the atmosphere and attempts have therefore been made to characterise them immediately following their preparation. In contrast, the 3-heteroaryl analogues are found to be more stable. $^{119m}Sn$ Mossbauer, $^{119}Sn$ nmr and mass spectrometry studies have been carried out and the results of these studies are discussed. Chemical characterisation has also been employed and results provided for derivatives of greater stability which can be more accurately analysed and characterised.

In Chapter 3 the solid state structures of tri(3-thienyl)tin bromide and its triphenylphosphine oxide adduct are reported and discussed in conjunction with previously obtained Mossbauer data.

An introduction to Mossbauer spectroscopy is provided in an appendix to this thesis.

# ACKNOWLEDGEMENTS

The author wishes to express her thanks to the SERC for a research studentship and to the International Tin Research Institute for their support in a CASE award. Particular thanks are due to Dr P J Smith and members of his department for their most informative counselling. I am indebted to Dr J S Brooks for his guidance with the Mossbauer Studies and to Dr I W Nowell and Miss L March for their considerable assistance with the crystallographic work. Many thanks to Mrs Mahala Titterton for her sterling efforts with the lion's share of the typing and also to Mrs Sharon Sedgewick and Miss Ann Hughes for their help with some of the sections. Special mention should also be made of my colleagues, friends and family for their support throughout my studies. Finally, I would like to reserve a very special thank you to my supervisor, Dr D W Allen, whose patience during the writing of this thesis must rival that of a saint. I wish to thank him for his critical appraisal of this thesis and for his guidance, encouragement, suggestions and tireless enthusiasm throughout the research programme.

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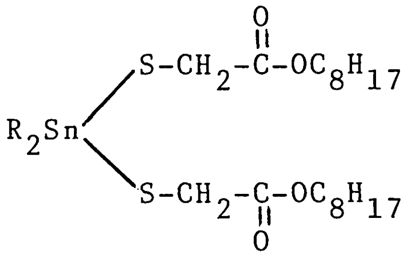
# CHAPTER 1: INTRODUCTION

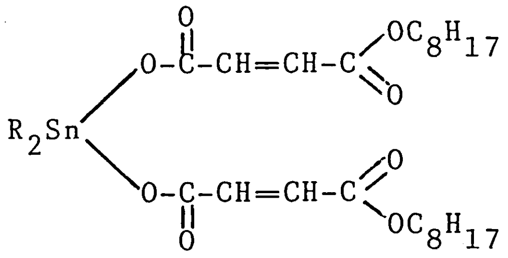
## 1.1 Uses of Organotin Compounds

Although the preparation of the first organotin compound was reported by Frankland in 1849[1] it is only within the last two decades that large scale industrial applications have emerged for this class of compound. Presently some 8-10Ktonnes of tin are consumed in their preparation each year, almost 6% of the total tin usage, and a number of factors are indicative of a future increase in this figure. In the environment, they are less damaging than other organometallic compounds, with the relatively weak tin-carbon bonds assisting degradation within the environment to essentially non-toxic inorganic tin species[2]. Additionally the organic compounds of tin are much more diverse in their applications than those of other metals, with the whole range of organotin derivatives, $R_4Sn$, $R_3SnX$, $R_2SnX_2$ and $RSnX_3$, being utilised. However, the di- and tri-organotin compounds predominate the application field.

Approximately two-thirds of the organotin compounds manufactured are employed in non-biological usage, these being largely the diorganotin derivatives. The largest single application of these is in the stabilisation of PVC. Degradation of the polymer by heat or extended exposure to light results in its discolouration and embrittlement which manifests itself in a loss of attractiveness and appeal to the customer. Additions of dialkyltin derivatives, at concentrations of 1-2% w/w, have been found to be most effective in maintaining the clarity and retarding the degradation of PVC. In general, dialkyltin bis(iso-octylthioglycolates) (1) are used to assist heat stability in initial processing, while dialkyltin bis(iso-octylmaleates) (2) prolong stability to light.



(1)



(2)

The very low toxicity of di(n-octyl)tin bis(iso-octylthioglycolates) (1,R=octyl), in particular, has resulted in their being approved for use in stabilising food-contact PVC packaging. The low mammalian toxity is attributed to an increased alkyl chain length (Table 1.1) and the introduction of two sulphur ligands which

TABLE 1.1

Acute, Oral Toxicities of Dialkyltin Dichlorides[3]

| R in $R_2SnCl_2$ | $LD_{50}$ (rats) (mg/kg) |
|---|---|
| Me | 74-237 |
| Et | 66-94 |
| $^{n}Bu$ | 112-219 |
| $^{n}Oct$ | 4000-7000 |
| $C_{16}H_{33}$ | 10,000 |
| $MeOCOCH_2CH_2$ | 2350 |

significantly reduce the possibility of interaction with sulphydryl groups in living systems[4].

A number of dialkyltin compounds act as curing agents for room-temperative vulcanising silicones e.g. dibutyltin dilaurate, and dibutyltin diacetate. The dialkyltin diester catalyst is added to the liquid silicone at room temperature, and the reactive carboxylate groups initiate cross-linking of the silicone producing a flexible elastomeric solid. Compounds of this type also catalyse the addition of alcohols to isocyanates producing rigid or flexible polyurethanes for modern furniture materials, surface coatings and cavity wall insulators.

The discovery that "cis-platin" (cis-dichlorodiammineplatinum (II), Fig 1.1A) exhibited anti-tumour activity[5] represented the first significant opportunity for the reintroduction into medicine of such metal complexes. More recently complexes of diorganotin dihalides with nitrogen or oxygen donor ligands, modelled on the originally active platinum compounds (Fig.1.1 A and B)[6], have also been found to exhibit anti-tumour activity [7,8]. Unlike platinum, tin does not form square plannar complexes, but prefers tetrahedral, trigonal bipyramidal or octahedral geometries[4]. Thus octahedral complexes of diorganotin compounds with either two monodentate or one bidentate ligand (e.g. Fig 1.1 C) were considered to be potentially active complexes. The diorganotin complexes chosen for testing contained cis-halogen groups, the cis positioning being an essential requirement for activity in the platinum analogues. Barbieri and co-workers[9] have found some diorganotin complexes of the biological molecules adenine and glycylglycine to be active against leukaemia, and two possible modes of action have been proposed. The complexed species may be preferentially transported to the tumour cells which are subsequently attacked by the biologically active diorganotin(IV) moiety produced from the hydrolysis of the adduct. Alternatively the diorganotin complexes may act as anti-metabolites. Although the tin analogues appear to be less active than "cis-platin", there is no evidence

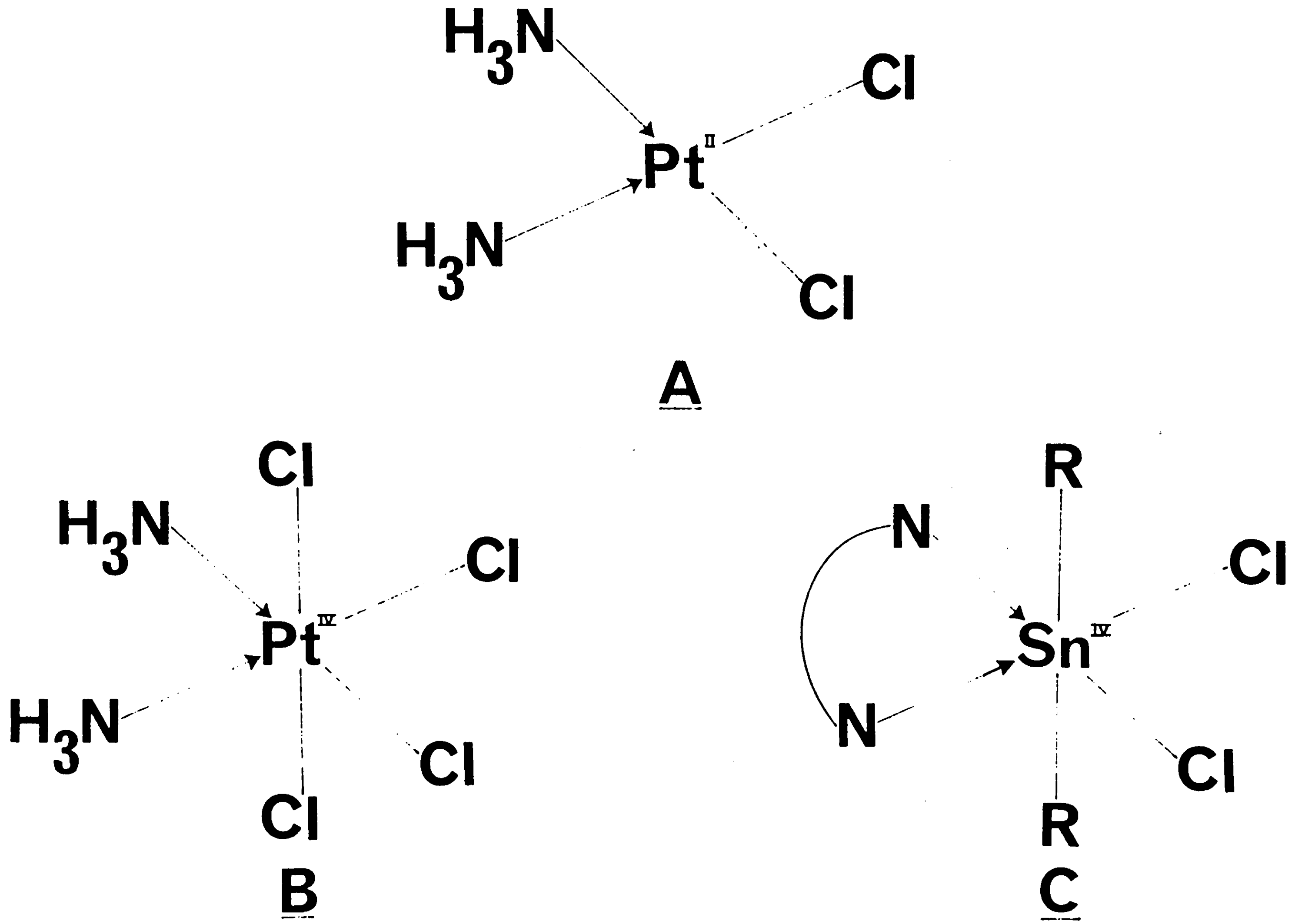


Figure 1.1

of the high nephrotoxicity displayed by some of the platinum complexes.

Applications are governed by a knowledge of structure-toxicity patterns for the organotin derivatives. The progressive introduction of organic groups at the tin atom produces a maximum biological activity against most types of living species when three organic groups are attached. Numerous biological applications have been found for triorganotin compounds. The level of toxicity for trialkyltin compounds is dependent upon the length of the alkyl chain (Fig.1.2)[4]. Triphenyl- and tricyclohexyltin derivatives are considered to have intermediate mammalian toxicity, comparable with that of their tri(n-butyl)tin analogues. Trimethyltin compounds display effective insect control but their application is restricted by high mammalian toxicity. In general the lower tri(n-alkyl)tin species (methyl-pentyl) exhibit high biological activity but also show high phytotoxicity. Propyl, butyl and pentyl groups can be seen to confer high fungicidal and bacterial activity. In all instances the anionic group attached to tin has little influence on the spectrum of biological activity, unless active in its own right. Of greater importance is the need for the anionic group to facilitate sufficient minimal solubility in the required solvent. Inorganic compounds of tin are orders of magnitude less toxic than the most potent organotin species. This is not

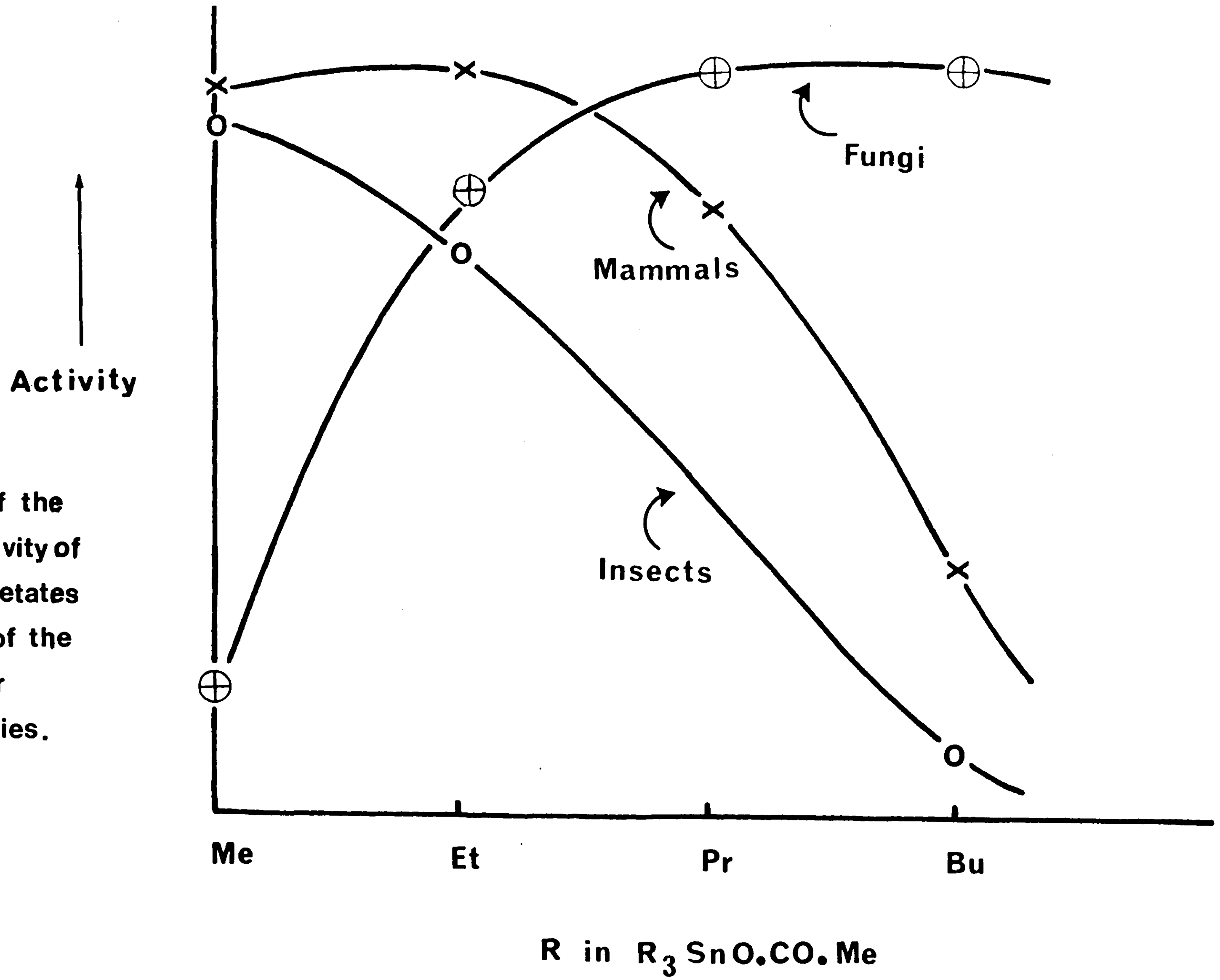
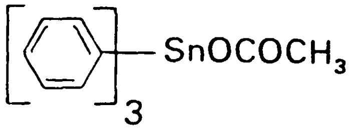


Figure 1.2
Dependence of the biological activity of tri-n-alkyltin acetates on the nature of the alkyl group for different species.

the case for other heavy metals previously employed as agrochemical agents and this has therefore been an important factor in the agricultural utility of organotin compounds.

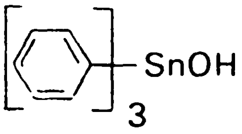
The organotin compounds presently employed as commercial pesticides are summarised in Figure 1.3. Triphenyltin compounds are highly toxic fungicides. In the 1960's triphenyltin acetate (Fig.1.3,(1)) was introduced in Europe for the treatment of potatoes (late blight) and sugarbeet fungi. Shortly afterwards triphenyltin hydroxide (Fig. 1.3, (2)), which displays a similar spectrum of disease control, was marketed in competition with the analogous acetate. Both compounds have, more recently, been found to deter insects from feeding. Antifeedants prevent the insect from recognising the normal host plant gustatory stimulus by inhibiting taste receptors. As indirect and more selective methods of pest control become more desirable in order to combat broad spectrum activity, persistance and resistance, the potential for triorganotins in the area is well recognised.

Tricyclohexyltin hydroxide (Fig. 1.3, (3)) is commercially available for the control of phytophagous by red spider mites on apples and pears. A good control of harmful arachnids is provided with little toxicity effects on beneficial insects such as honey bees. Tricyclohexyl- and tricycloheptyltin compounds are essentially



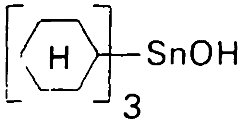
Fentin acetate (Brestan)
(Höechst)
mp 118–120°
LD$_{50}$(rats) 125 mg/kg

(1)



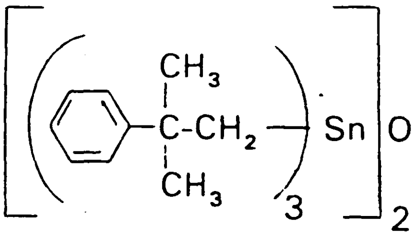
Fentin hydroxide (Du-Ter)
(Philips Duphar)
mp 116–120°
LD$_{50}$(rats) 108 mg/kg

(2)



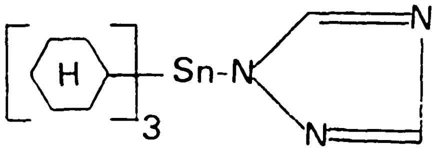
Cyhexatin (Plictran)
(Dow)
mp 195–198°
LD$_{50}$(rats) 540 mg/kg
LD$_{50}$(bees) 32 µg/bee

(3)



Fenbutatin Oxide (Vendex)
(Shell)
138–139°
LD$_{50}$(rats) 2,630 mg/kg
LD$_{50}$(bees) 100 µg/bee

(4)



Azocyclotin (Peropal)
(Bayer)
mp 218·8°
LD$_{50}$(rats) 631 mg/kg

(5)

**Figure 1.3 Organotin pesticides used in agriculture**

non-phytotoxic and there is no evidence, at present, for any immunity having developed or for their degradation to any long-lasting harmful residues. Triphenyl- and tricyclohexyltin derivatives are easily broken down by the combined action of light and microorganisms[10,11] with stepwise cleavage of organic groups[12], leading to inorganic tin species, which are not taken up by plants.

Tributyltin derivatives have shown a high antibacterial activity, particularly against Gram-positive bacteria. This has led to their use in disinfectants, usually in conjunction with a chemical capable of acting as a toxicant towards Gram-negative bacteria.

Bis(tri-n-butyltin) oxide (TBTO, (3)) has proved very effective in protecting cellulosic materials against fungal

$$(Bu_3\,Sn)O(Sn\,Bu_3)$$

(3)

attack. In wood preservation, TBTO is thought to react rapidly with carbon dioxide trapped in the wood, to form bis(tributyltin)carbonate. High retention of the organotin species within the cellulosic material has been attributed to the polymeric self-associating nature of the resultant carbonate[4]. Impregnation of tributyl- and triphenyltin derivatives into cellulose and woollen fabrics has afforded some protection of the cloth against fungal attack and destruction by moths. The bulky triorganotin moieties are thought to block reactive sites within the fabric[13].

A rapidly growing application of triorganotin compounds is their role in marine anti-fouling paints. Tributyl- or triphenyltin derivatives are gradually released from the paint into the water where they act as toxicants towards marine growths whilst being non-corrosive towards the hull of the vessel. The lifetime of these coatings has been successfully extended by incorporation of the organotin agent into a polymeric network. The controlled release of the organotin species from the rubber or polymer matrix has rendered such formulations much more cost effective. These materials may also be valuable in the control of water-borne tropical diseases such as bilharzia, since the slowly released trialkyltin derivative is capable of destroying the intermediate snail hosts[14,15].

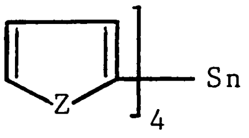
Monoorganotin derivatives have yet to find extensive commercial utilisation. However, certain monoorganotin compounds (e.g. $BuSn(IOTG)_3$ ) are used in conjunction with corresponding dialkyltin stabilisers in rigid PVC, and the introduction of around 30% of the monoorganotin has been found to give the optimum synergistic improvement in stabilisation[4].

Tetraorganotin compounds, e.g. tetraphenyltin, tetrabutyltin, serve largely as intermediates in the preparation of lower organotin compounds. There are, however, one or two minor industrial applications, e.g. as acid scavengers and corrosion-inhibiting additives in lubricating oils. Both tetra- and monoorganotin species possess intrinsically low toxicities and this may well

## 1.2 Electronic Properties of Heterocyclic Substituents

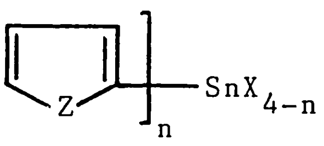
In view of the increasing number of applications for organotin chemicals it is perhaps rather surprising that relatively little has been reported on the chemistry of related organotin compounds bearing heteroaryl substituents, in which the heteroaryl group is bound to tin via a carbon of the heterocyclic ring. The variation in electronic character which can be obtained by using heterocyclic substituents might be expected to influence the structure and reactivity of the proposed organotin species and therein provide some new and potentially useful properties.

A number of symmetrical and unsymmetrical tetraorganostannanes bearing heteroaryl substituents have been described. However publications concerning heteroaryltin derivatives of the type $R_nSnX_{(4-n)}$, where R= heterocyclic substituent, X = univalent anionic group and n = 1 - 3, are very scarce and rather vague [16 - 21]. The proposed initial course of the present investigation was to prepare the synthetically accessible tetra (2-thienyl) - and tetra (2-furyl) tins (4) which were then to be treated with reagents previously employed in the chemistry of phenyltin compounds, in order to prepare the desired range of di- and



(4)

Z=S or O



(5)

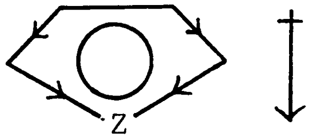
Z=S or O

X=Halogen or any suitable univalent anionic group

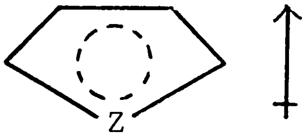
n=2 or 3

triheteroaryltin derivatives, (5). Following chemical and analytical characterization it was envisaged that these compounds (5) and their complexes would be suitable for evaluation as pesticides, polymer stabilisers and anti-cancer agents respectively.

The effect of the heterocyclic groups on the stability and reactivity of such organotin derivatives will depend on the relative contributions of the $\pi$ and $\sigma$ electron systems of the rings.

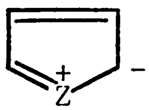


inductive effect

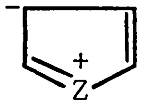


mesomeric moment

By virtue of their chemical reactivity, furan and thiophen have been labelled as "electron-rich aromatics". Electrophilic attack does not occur at the lone pair on the heteroatom, the donation of two electrons to the aromatic sextet leaving the heteroatom bearing a partial positive charge and the ring carbons partially negative. This charge distribution also follows from the valence bond theory as a consequence of contributions of the resonance hybrids of canonical forms (6) and (7). The

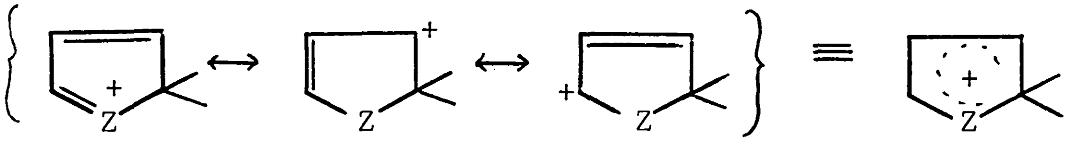


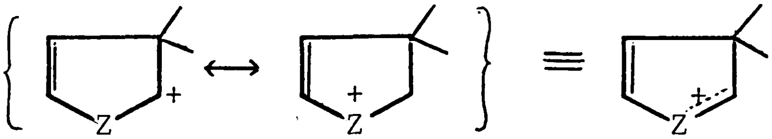
(6)



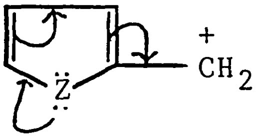
(7)

release of electrons from the heteroatom facilitates a high degree of reactivity towards electrophilic substitution at the ring carbon atoms, especially the 2-position. The preference may be due to the number of contributory canonical forms for the intermediate cation; attack at the 2-position gives rise to three possible canonical forms while reaction at the 3-position yields only two[22].





A summary of the data available on the relative reactivities of these systems in electrophilic substitution[23] revealed the following observed order of reactivity:- furan > thiophen > benzene. It was suggested, however, that the ease of electrophilic substitution of these compounds is not of necessity an indication of an increased ground-state electron density at the ring carbon atoms, since the reactivity data refers to the reactants and the transition states. The most widely accepted mechanism for electrophilic aromatic substitution involves a change from $sp^2 \longrightarrow sp^3$ hybridisation for the carbon under attack, with the formation of a Wheland intermediate, the electron rich heterocycle having the apparent ability to stabilise the electron deficient intermediate. Furthermore, the halogenomethyl derivatives of these systems are very readily hydrolysed in comparison with their benzyl halide analogues[24]. This feature may be understood by considering the resonance stabilisation of the intermediate carboniom ion (8) in terms of $p\pi \longrightarrow p\pi$ overlap between the ring and the carbonium ion centre. It may therefore be possible that the presence of such heteroaryl groups at tin could reduce the Lewis acidity of compounds of the type $Ar_2SnX_2$ by $p\pi \longrightarrow d\pi$ overlap with the tin atom and thereby aid stabilisation.



(8)

As an extension to a detailed study of substituent effects on the intensity of the C≡N stretching vibration of a series of benzonitriles, Deady and co-workers[25] investigated the 2- and 3-cyanoderivatives of furan and thiophen. A series of substituent ($\sigma^+$) constants were obtained and compared with those from electrophilic substitution reactions. In each case the heterocycle appeared to act as an electron donor. However greater electron donation was observed by the 2- and 3- thienyl substituents than for the corresponding furyl groups, a reversal of their ease of electrophilic substitution.

In addition to their ability to function as "electron-rich" species, the furyl and thienyl groups are capable of acting as electron withdrawing substituents, due to the effect of the electronegative heteroatom withdrawing electrons via an inductive mechanism. For example, from studies of the chemistry of heteroarylphosphorus compounds[26,27], it has been concluded that the 2-furyl and 2-thienyl groups behave as moderately strong electron withdrawing substituents when attached directly to phosphorus.

Evidence that the 2-furyl and 2-thienyl substituents are more electron-withdrawing than phenyl in their inductive effect has also been obtained from a study of carboxylic acid pKa data. The pKa data (Table 1.2) show that 2-thiophen carboxylic acid and furoic acid are

Table 1.2

Ionisation constants of carboxylic acids in water at 26°C.

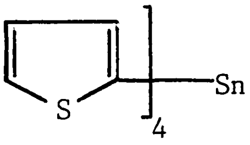
| Acid | pKa | ref |
|---|---|---|
| Benzoic acid | 4.21 | 28 |
| 2-Furoic acid | 3.16 | 29 |
| 3-Furoic acid | 3.95 | 30 |
| 2-Thiophen carboxylic acid | 3.53 | 29 |
| 3-Thiophen carboxylic acid | 4.10 | 31 |

stronger acids than unsubstituted benzoic acid. It is noteworthy that the 3-thiophen and 3-furan carboxylic acids are significantly weaker than those of the corresponding 2-position, presumably a direct consequence of the increased displacement of the carboxy group from the electronegative heteroatom.

The high reactivity of furan and thiophen towards electrophilic substitution led to the original assumption that the dipole moment in these heterocycles was from the heteroatom to the ring. However it is now widely accepted that the dipole moment lies in the opposite direction i.e. from the ring to the hetero atom[32]. Thus, if $p\pi \longrightarrow d\pi$ interactions are not possible between the ring and vacant d-orbitals at tin, it would appear that the properties of heteroaryl tin derivatives might well be dominated by the electron-withdrawing effects of the heterocyclic substituents.

## 1.3 Survey of Literature Relating to Heteroaryltin Compounds

Tetra(2-thienyl)tin (9) has been known for a number of years and was first prepared in 1927 by Krause and Renwanz[33]. The Grignard reagent derived from 2-iodothiophen was treated with tin(IV) chloride. Subsequently the same authors effected the preparation of the mixed arylstannane, triphenyl(2-thienyl)tin(10), by replacing tin(IV) chloride with triphenyltin bromide in the above synthesis[34].



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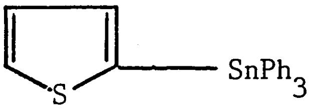
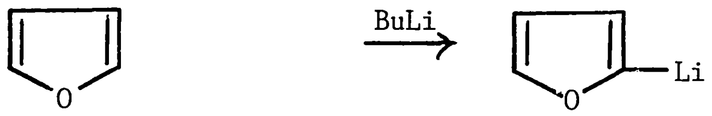
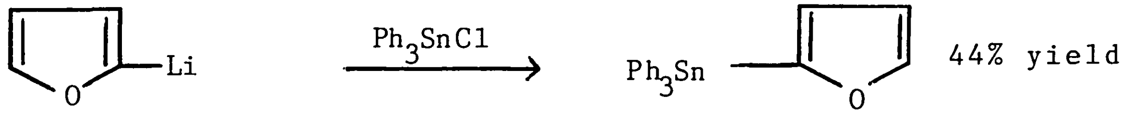


(10)

The first reported organotin compound incorporating the 2-furyl substituent was triphenyl-(2-furyl)tin (11), prepared by Gilman and Goreau from 2-furyl lithium[35]:



followed by



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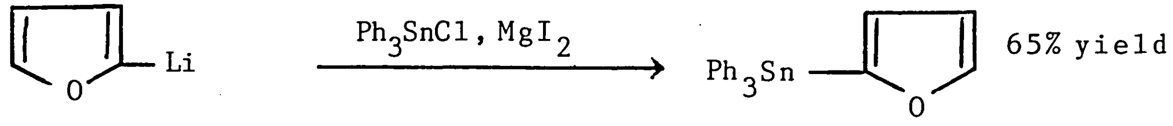
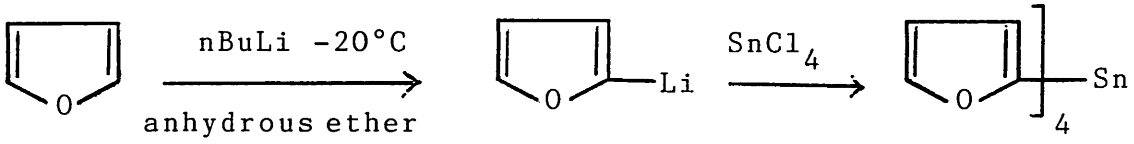


(11)

It was not until 1971, almost 20 years later, that the symmetrical tetraheteroarylstannane, tetra(2-furyl)tin (12), was isolated by Barbieri and Taddei[36]. This publication also outlined the synthesis and characterisation of the previously unreported tetra(3-furyl)tin (13) and tetra-(3-thienyl)tin (14) as well as an alternative route to tetra-(2-thienyl)tin, involving direct metallation of thiophen.

### Tetra (2-furyl)tin



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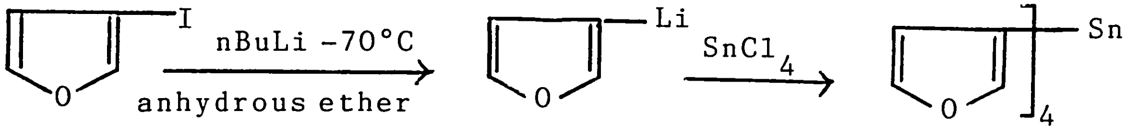
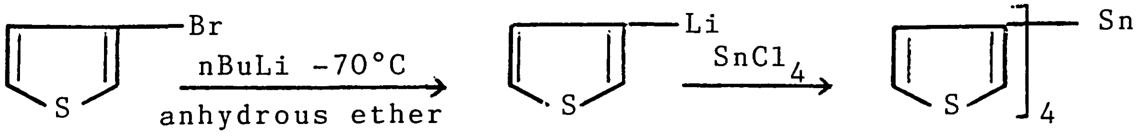
### Tetra(3-furyl)tin



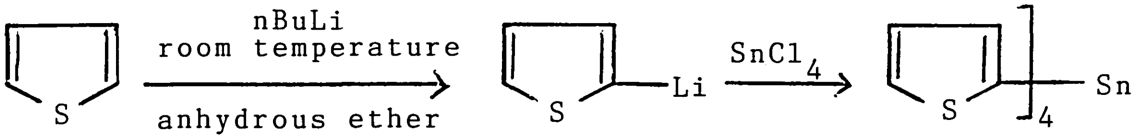
(13)

Tetra(3-thienyl)tin



(14)

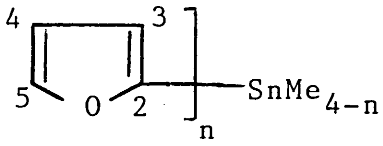
Tetra(2-thienyl)tin



(9)

A study of the $^{1}$H nmr spectra of these compounds, and particularly the $^{117}$Sn and $^{119}$Sn satellite bands, facilitated the determination of the long range $^{117,\ 119}$Sn—$^{1}$H coupling constants which may provide information on the electronic distribution of the heterocyclic moiety, the nature of the metal-organic bond and the hybridisation of the metal bonding orbitals. The proton chemical shifts appeared to indicate that some degree of $p\pi \rightarrow d\pi$ bonding is present between the empty d orbitals of tin and the $\pi$ - system of the heteroaryl group. This suggestion was revised in a later paper, by the same authors[37], reporting the observation of $^1H$ nmr spectra of triheteroarylmethyltin derivatives and stating that such $p\pi \rightarrow d\pi$ effects should be small, the nmr parameters mainly being influenced by the inductive effect from the unsaturated system. The observation of larger J (Sn-C-H) coupling constants for the furyl derivatives than for thienyl and phenyl analogues was attributed to the presence of oxygen resulting in an increased electronegativity for the heterocyclic substituent.

Results obtained by Doddrel et al[38] from $^{13}C$ nmr studies of some phenyl, furyl and thienyl organometallics are consistent in that they produced no conclusive evidence for $p\pi \rightarrow d\pi$ interactions between the ring system and the metal. For mixed arylmethylstannanes, a large increase in $J(^{119}Sn — ^{13}C)$ was observed as the number of furyl groups surrounding tin was increased. Coupling constants were found to be larger than those for the corresponding thienyl compounds and considerably larger than those for the phenyl derivatives. The authors postulated that this may be due to the polar nature of the furyl ring increasing the effective nuclear charge at tin, thus suggesting that differences in the $^{13}C$—metal coupling constants may not solely be due to changes in the '<u>s</u>' -character of such bonds. A later paper by Lippmaa and co-workers[39] discussing the $^{13}C$ and $^{119}Sn$ nmr spectra of mixed methyl and 2-furyl stannanes (15), noted that the deshielding of the aromatic ring atoms was accompanied by a strong diamagnetic shielding

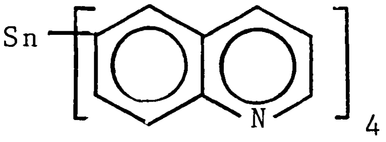


where n=1-4

(15)

of the tin atom. On increasing the number of furyl substituents, the increased deshielding of ring atoms C3, C4 and C5 was essentially linear. However the diamagnetic shielding of the central atom increases much more than is expected from simple additivity and is also much larger than in the case of the corresponding phenyl compounds. This pattern was tentatively attributed to an increased migration of electronic charge towards vacant '<u>d</u>' orbitals when the number of furyl groups increases. Most recently Erchak and co-workers have reported multinuclear nmr data for a series of mixed stannanes, bearing methyl and 3-furyl groups[40], prepared from the reaction of 3-furyl lithium with the appropriate methyltin(IV) chloride.

Mössbauer data have been reported for tetra(2-furyl)tin and tetra(2-thienyl)tin[41] but not for the related 3-heteroaryl derivatives. In addition to these four compounds the only other symmetrical tetraheteroarylstannanes reported are tetra(6-quinolyl)tin (16) and tetra(2-quinolyl)-tin (17)[42]. In addition to outlining preparative routes to these and other



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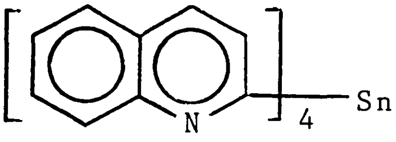
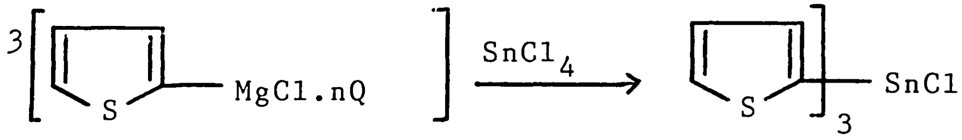


(17)

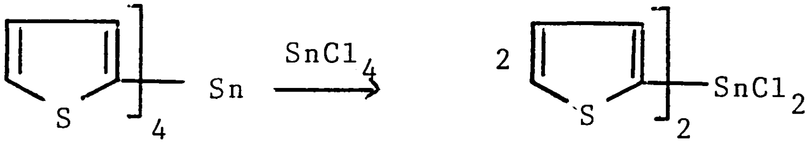
tetraarylstannanes, including tetra(2-thienyl)-tin, the same patent[42] claims the preparation and isolation of the corresponding tri-, di- and monoheteroaryltin chlorides by similar processes, involving the preparation and reaction of a suitable heteroaryl Grignard reagent with an appropriate molar ratio of tin(IV) chloride e.g.,



Q = cyclic ether, also used as solvent

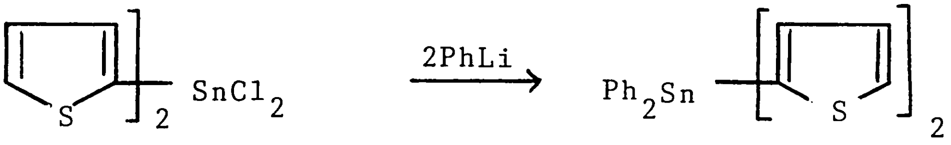
For these compounds, however, physical and analytical data are conspicuous by their absence, and these derivatives can in no way be said to have been characterised.

Previously Bobasinskaja and Kozeschkow[43] had reported the preparation of di(2-thienyl) tin dichloride (18) via a redistribution reaction between tetra(2-thienyl)tin and tin (IV) chloride:

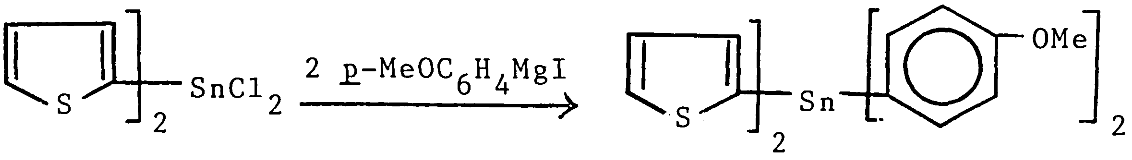


(18)

This was followed by immediate chemical characterisation of the product with phenyl lithium or a para-methoxyphenyl Grignard reagent. However, in both cases only % Sn figures were provided and melting point ranges were somewhat large.

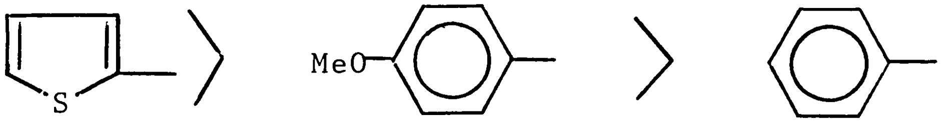


30% yield



18% yield

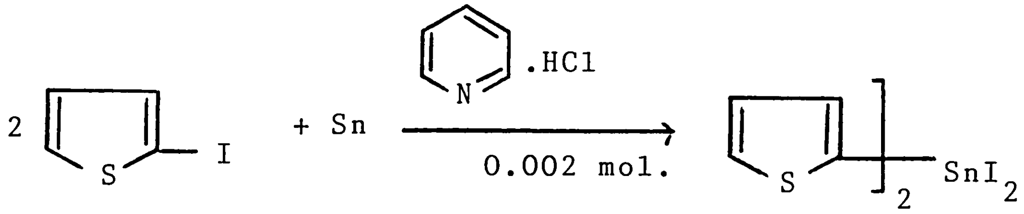
On treatment of these stannanes with hydrochloric acid, the following order of group cleavage was observed:



Thus the more electronegative 2-thienyl group is most readily cleaved, consistent with its greater ease of electrophilic substitution.

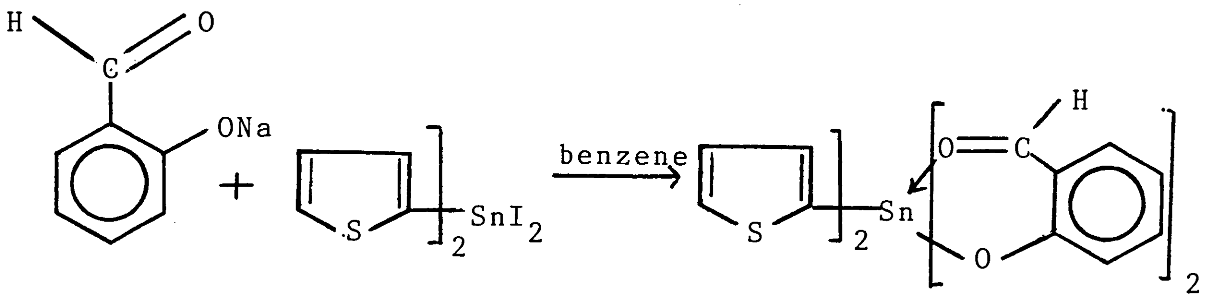
The $^{119}$Sn chemical shift of di(2-thienyl)tin dichloride was reported in a later paper by Tupciauskas and co-workers[44].

Gopinathan et al have prepared di(2-thienyl)tin diiodide (19) by the oxidative addition of 2-iodothiophen to tin metal in the presence of an appropriate catalyst[45].



(19)

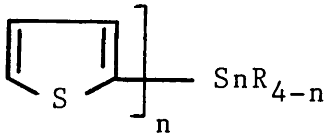
The iodine atoms were subsequently replaced by chelating ligands such as salicylaldehyde, dibenzoylmethane, benzoylacetone, acetoacetanilide, 8-hydroxyquinoline and diphenyldithiophosphinic acid via reaction of the sodio derivative of the ligands in benzene to give 6-coordinate tin complexes e.g (20)



(20)

A private communication[46] referring to some unpublished studies relates difficulties experienced when attempting to prepare tri(2-furyl)tin halides. Disproportionation of tetra(2-furyl)tin with tin(IV) chloride at 200°C resulted in only a very low yield of impure product. In general the tri(2-furyl)tin halides proved to be unstable towards air and water and could not be converted to the corresponding hydroxides and acetates. Tetra(2-thienyl)tin could not be converted to stable tri(2-thienyl)tin derivatives.

Almost all the other papers concerned with heteroaryltin compounds involve studies of unsymmetrical tetraorganostannanes. Gopinathan and co-workers[47] have prepared a series of mixed stannanes (21) from the reactions of (2-thienyl)magnesium



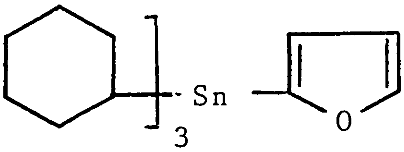
where R = Bu or Ph

n = 4,2 or 1

(21)

iodide with tin(IV) chloride (for tetra(2-thienyl)tin) or the appropriate organotin chloride. The reported derivatives appeared to show similar properties to their phenyl analogues and were quite stable. These compounds were also reported to undergo reactions with sulphur dioxide at $-20^{\circ}C$ to give products which were assumed to involve insertion of $SO_2$ into the Sn - C bond.

In 1972, the Dow Chemical Company patented the preparation of some cyclic substituted derivatives of tricyclohexyltin[48], including (2-furyl)tricyclohexyltin (22), (2-pyridyl)tricyclohexyltin (23) and (3-pryridyl)tricyclohexyltin (24).



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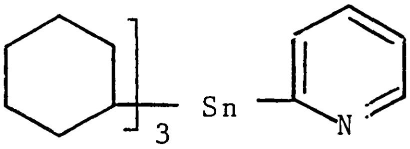

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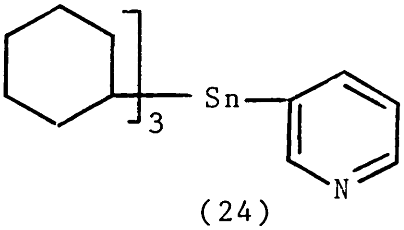
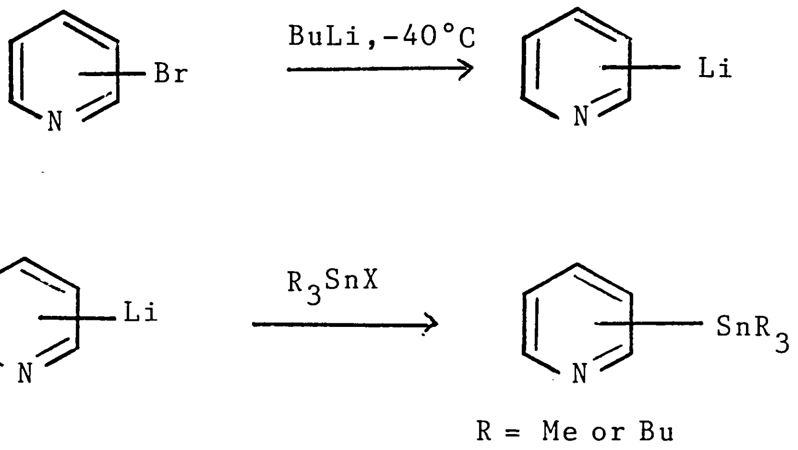


(24)

These compounds were thought to be of potential use to the agrochemical industry and preparation was effected by reaction of a heteroaryl sodium reagent with tricyclohexyltin chloride.

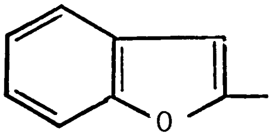
In the course of experiments to prepare compounds containing the (2-pyridyl)- tin linkage, tributyl-(2-pyridyl)tin was prepared from (2-pyridyl)magnesium bromide and tributyltin chloride by McWhinnie et al[49]. Triphenyl(2-pyridyl)tin, however, could not be isolated by the same method. Further preparations of mixed stannanes (25) involving pyridyl substituents have been achieved by Mitchell[50].



(25)

Dibutylbis(pyridyl)tins and butyltris(pyridyl)tins have also been prepared by the same method using dibutyltin dichloride and butyltin trichloride respectively. The $^{1}H$ and $^{13}C$ nmr data for the previously unreported trialkyltin and trialkyllead derivatives were compared with results for silyl and germyl analogues.

Eaborn and co-workers[51] have employed a series of aryltrimethyltin compounds as reagents for the formation of heteroaryl-transition metal bonds via electrophilic aromatic substitution reactions. The aryl substituents used were; 2-furyl, 2-thienyl, 2-benzo(b)furyl (26), 2-benzo(b)thienyl (27), phenyl and substituted phenyls.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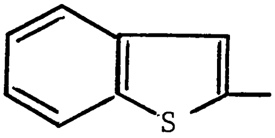
(27)

It was noted that the heteroaryltin compounds were more reactive than the phenyl derivatives, their reactions being complete at room temperature within a few hours.

e.g.

$[PtCl_2(COD)] + ArSnMe_3 \longrightarrow [PtClAr(COD)] + SnClMe_3$

$[PtClAr(COD)] + Ar'SnMe_3 \longrightarrow [PtArAr'(COD)] + SnClMe_3$

COD = cycloocta - 1,5- diene

There would appear to be no reports of the preparation of tetra(2-benzo(b)thienyl) - and tetra (2-benzo(b)furyl)tin or any of their derivatives.

Most recently, Jutzi and Gilge[52,53] have prepared a series of 2-heteroaryltrimethylstannanes derived from the reactions of the lithiated heterocycles, benzoxazole, benzothiazole, N-methylbenzimidazole, N-methylimidazole, N-methyltriazole, pyridine, quinoline and thiazole with trimethyltin chloride.

There is therefore a need to develop the chemistry of heteroaryltin halides of type (5) which might then be easily converted to derivatives of potential use as agrochemicals, polymer stabilisers and anti-cancer agents. This Thesis describes the preparation, characterisation and studies of the reactions of such compounds and also of the related 3-thienyl and 3-furyl analogues. Characterisation has been effected by employing microanalytical techniques, $^{119}$Sn Mossbauer and nmr spectroscopy and in specific cases X-ray diffraction methods. In instances where instability has precluded elemental microanalysis, attempts have been made to characterise such compounds by the formation of stable complexes or other appropriate derivatives.

An introduction to Mössbauer Spectroscopy is given in an appendix to this Thesis.

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# CHAPTER 2: THE PREPARATION AND CHARACTERISATION OF SOME HETEROARYLTIN COMPOUNDS

## 2.1 Synthetic Routes Based on the Chemistry of Phenyltin Analogues

The organotin halides and, in particular, the organotin chlorides, occupy a central position in organotin chemistry being used as intermediates for the preparation of a wide range of organotin derivatives (Scheme 2.1.1)[1]. Thus the preparation of some di- and triheteroaryltin halides was considered to be of singular importance in the route to some potentially useful heteroaryltin compounds.

Commonly, organotin halides are prepared from tetraorganotin compounds. The principal methods for the formation of tetraorganotins involve the reaction of an organometallic reagent with a tin (IV) derivative, frequently tin (IV) chloride.

i.e. $SnCl_4 + 4RM \longrightarrow R_4Sn + 4MCl.$

Three major reactions of this type employed on a commercial basis are the Grignard, Wurtz and Aluminiumalkyl procedures[2].

Grignard:

$SnCl_4 + 4\ RMgCl \longrightarrow R_4Sn + 4MgCl_2$

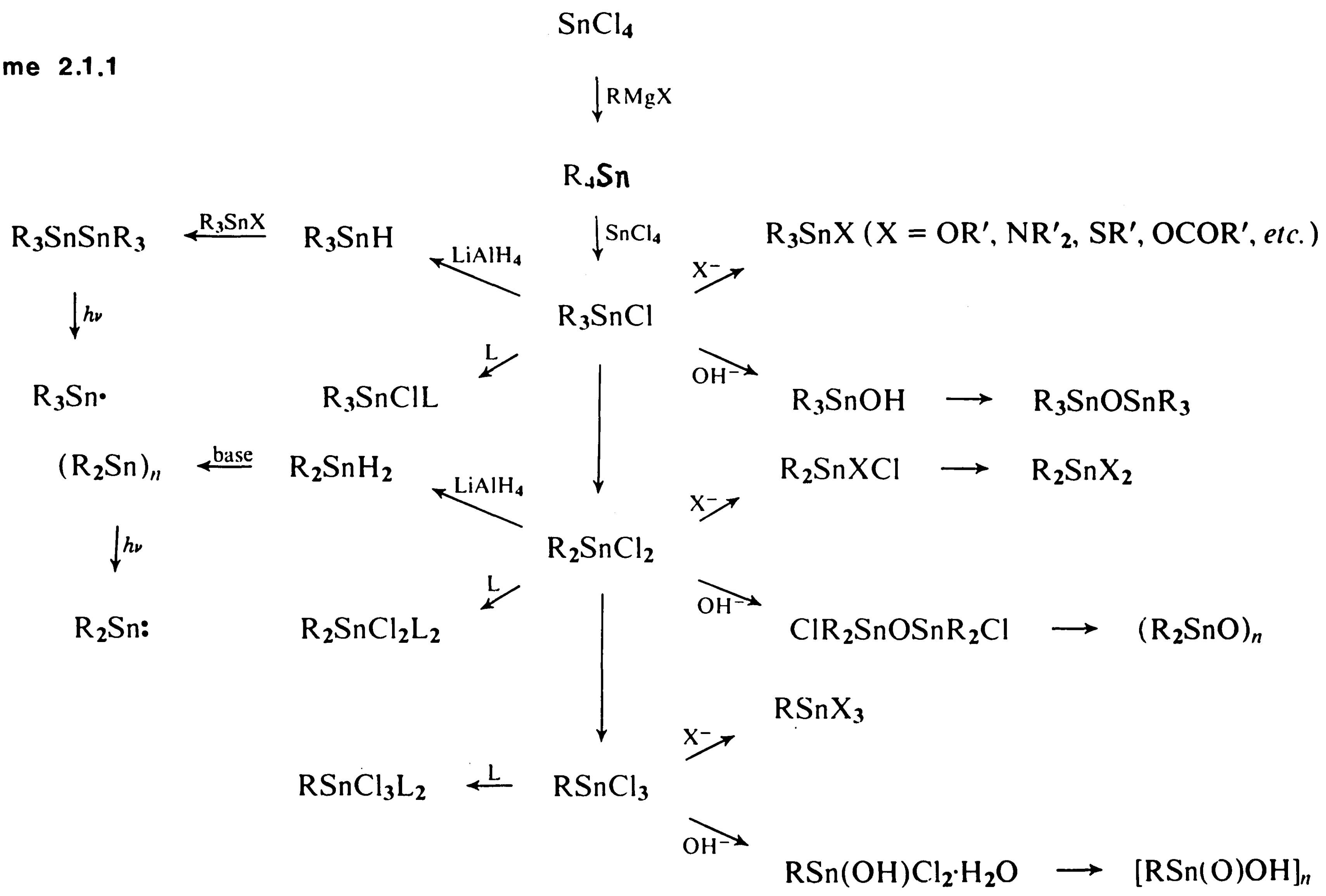
Wurtz:

$SnCl_4 + 4RCl + 8Na \longrightarrow R_4Sn + 8\ NaCl$

Aluminium alkyl:

$3\ SnCl_4 + 4\ R_3Al \longrightarrow 3\ R_4Sn + 4AlCl_3$

To date, for the commercial manufacture of tetraphenyltin, (R=phenyl), only the Grignard method appears to be useful. However, for research purposes, Scheme 2.1.1


SnCl4
RMgX
R4Sn
SnCl4
R3SnCl
R2SnCl2
RSnCl3
LiAlH4
L
X−
OH−
R3SnSnR3
R3SnX
R3SnH
hν
R3Sn•
R3SnClL
(R2Sn)n
base
R2SnH2
R2Sn:
R2SnCl2L2
RSnCl3L2
R3SnX (X = OR′, NR′2, SR′, OCOR′, etc.)
R3SnOH
R3SnOSnR3
R2SnXCl
R2SnX2
ClR2SnOSnR2Cl
(R2SnO)n
RSnX3
RSn(OH)Cl2·H2O
[RSn(O)OH]n

the reaction of tin (IV) chloride with organolithium reagents has also been well favoured for the preparation of tetraaryltin compounds. More recently Nicholson and coworkers[3] have developed a new direct route to tetraorganotin compounds from metallic tin:-

$$4\ RX + Sn + 2Zn \xrightarrow[160 - 170^{o}C]{Bu_4NI} R_4Sn + 2ZnX_2$$

However, chlorobenzene fails to undergo this reaction, thus showing this particular method to be unsuitable for the synthesis of tetraphenyltin and probably also for tetraaryltins in general.

One very important route to organotin halides involves the redistribution reactions of the above tetraorganotin compounds with anhydrous tin (IV) halides[4]. The preparation of tri-, di- and mono-organotin chlorides can be achieved by employing the following reactions:

$$3R_4Sn + SnCl_4 \longrightarrow 4R_3SnCl \qquad (i)$$

$$R_4Sn + SnCl_4 \longrightarrow 2R_2SnCl_2 \qquad (ii)$$

$$R_4Sn + 3SnCl_4 \longrightarrow 4RSnCl_3 \qquad (iii)$$

The initial reaction between tin (IV) chloride and the tetraorganotin (equation iv) proceeds very rapidly at room temperature.

$$R_4Sn + SnCl_4 \xrightarrow[Temperature]{Room} RSnCl_3 + R_3SnCl \qquad (iv)$$

At elevated temperatures, if equimolar quantities of the two starting materials are used, the second step furnishes the dichloride (equation v).

$$RSnCl_3 + R_3SnCl \xrightarrow[200^{\circ}\ C]{} 2R_2SnCl_2 \qquad (v)$$

However, if the tetraorganotin is in excess (equation i) it then reacts further with the diorganotin dichloride formed in the two intermediate steps (equation v and vi) to yield the triorganotin halide (equation vii)

$$R_4Sn + RSnCl_3 \longrightarrow R_2SnCl_2 + R_3SnCl \qquad (vi)$$

$$R_4Sn + R_2SnCl_2 \longrightarrow 2R_3SnCl \qquad (vii)$$

Should the tin (IV) chloride be in excess (equation iii) this reacts with the initially formed triorganotin chloride (equation iv) to give a mixture of the di- and mono-organotin chlorides (equation viii).

$$R_3SnCl + SnCl_4 \longrightarrow RSnCl_3 + R_2SnCl_2 \qquad (viii)$$

For phenyltin chlorides[5] further reaction between diphenyltin dichloride and tin (IV) chloride is possible (equation ix)

$$Ph_2SnCl_2 + SnCl_4 \longrightarrow 2PhSnCl_3 \qquad (ix)$$

For alkyltin halides this reaction is extremely slow and as a result the partial stages of this reaction (equations iv or x) are usually employed in the industrial manufacture of alkyltin trichlorides, separation normally being achieved by distillation <u>in vacuo</u>.

$$R_4Sn + 2\ SnCl_4 \xrightarrow{100^\circ C} 2RSnCl_3 + R_2SnCl_2 \qquad (x)$$

A number of inorganic halides have been found to cleave bonds of tetraorganostannanes. Although these reactions are of only limited preparative importance, they have provided useful information about the reactivity of the Sn - C bond. In an alkaline medium, mercury (II) chloride is reported to successively replace phenyl groups in tetraphenyltin [6,7] whereas no reaction is observed with tetrabenzyltin[8]. Similar reactions between salts and tetraalkylstannanes are well documented; thus the reaction of tetraethyltin with mercury (II) chloride has been found to proceed almost exclusively to give ethylmercury (II) chloride and triethyltin chloride [9]:-

$$Et_4Sn + HgCl_2 \longrightarrow EtHgCl + Et_3SnCl.$$

Abraham and Andonian-Haftvan[10] found in the reactions between benzyltrialkylstannanes (where alkyl = $^nBu$, $^nPr$ and Et) and mercury (II) salts in methanol, only the benzyl group was cleaved to form a benzylmercury (II) compound. However, with benzyltrimethyltin, only a methyl group was removed. On the basis of this and previous work the following sequence of reactivity of alkyl/aryltin groups towards mercury (II) chloride and acetate was postulated:-

$$R = Ph > Me > PhCH_2 > Et > {}^nPr > {}^nBu$$

Contrary to earlier reports [11,12] the methyl group was also found to be preferentially cleaved in DMSO.

During an investigation into substituent effects on aryl-tin cleavage in aryltriethyltin compounds by mercury (II) acetate, Hashimoto and Morimoto[13] isolated only triethyltin acetate and phenylmercury (II) acetate from a reaction mixture of mercury (II) acetate and triethylphenyltin.

In addition to studies concerned with the reactivity of tetraorganotin compounds towards mercury (II) salts, many other metal halides have been employed and their reactivity, particularly towards tetraethyltin, investigated[14]. Commonly, the major reaction product was found to be the triethyltin halide. However, reaction with thallium (III) chloride yields mainly the diethyltin dichloride, while the same reaction with tetraphenyltin produces a mixture of the di- and triphenyltin chlorides[15].

Some early work by Bost and Borgstom[16] on the use of tetraphenyltin as a phenylating agent comments on the violent reaction of bromine and chlorine with tetraphenyltin. These reactions were found to produce excellent yields of the corresponding monohalides of benzene. No halogen disubstituted products of benzene were detected. The same reaction using iodine was found to be less active and resulted in only low yields of iodobenzene. Iodine monochloride, however, reacted very readily and produced a good yield of iodobenzene. Reactions of this type have since been employed by Krause[17] with a view to preparing the triphenyltin halides rather than the benzene derivatives. In general the reaction of a tetraorganostannane with one mole of halogen results in the formation of a triorganotin halide:-

$$R_4Sn + X_2 \longrightarrow R_3SnX + RX$$

Most commonly, bromine and iodine are employed. Reactions with bromine are normally conducted at $0^{o}C$ or below, in carbon tetrachloride, with the halogen being added very slowly to the tetraorganotin in order to minimise formation of the diorganotin dibromide. Tetraaryltins react very readily with a second mole of bromine at low temperatures, again in carbon tetrachloride, to form diaryltin dibromides. However, with iodine, even at elevated temperatures, only the monoiodide is attainable[17].

Tin-carbon bonds in tetraorganotin compounds may also be cleaved by hydrogen halides, either in solution or in the gas phase. Either the monohalides or the dihalides may be prepared by this route, depending on the reaction conditions employed[18].

e.g.

$$Ph_4Sn + HCl \longrightarrow Ph_3SnCl + PhH$$

$$Ph_4Sn + 2HCl \longrightarrow Ph_2SnCl_2 + 2\ PhH$$

One advantage of using this particular method is the production of a volatile hydrocarbon as by-product which can easily be removed from the reaction mixture.

Frankland's preparation of the first organotin compound[19], diethyltindiiodide (1), was achieved by direct synthesis from tin metal and ethyl iodide.

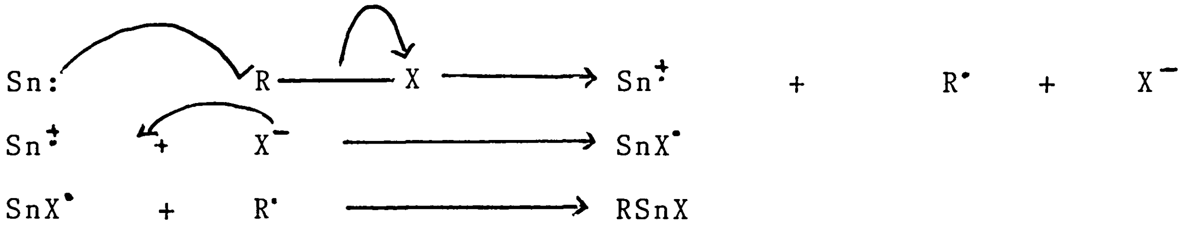
$$2\ \mathrm{EtI} + \mathrm{Sn} \longrightarrow \mathrm{Et_2SnI_2} \qquad (1)$$

Oxidative addition to tin has obvious attractions commercially as a solvent is not normally required, although a small amount of catalytic material e.g., quaternary or trialkyl derivative of group V, is usually essential. However the reaction does have certain limitations in that the dominant product tends to be the diorganotin species. The reactivity of organic halides towards tin in these reactions has been found to be RI>RBr>RCl[1].

The mechanism for the direct reaction[20] is thought to involve an initial activation, by the catalyst, of the carbon-halogen bond in the alkyl halide, facilitating reaction with metallic tin to form a tin (II) intermediate.

$$\mathrm{R{-}X} \xrightarrow[\mathrm{R^1{}_3M}]{\mathrm{R^1{}_4MY}} \begin{array}{l} \mathrm{R^1{}_3MR}\ \dots\dots\dots\mathrm{X} \quad + \mathrm{R^1Y} \\ \mathrm{R^1{}_3MR}\ \dots\dots\dots\mathrm{X} \end{array}$$

M = N, P or Sb

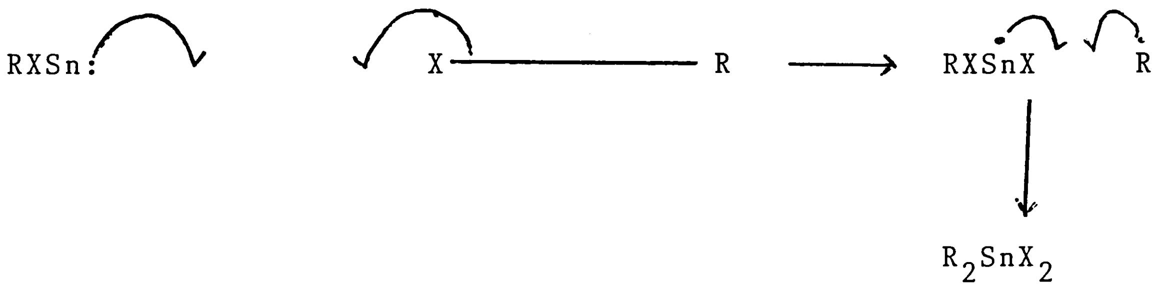


$$\mathrm{Sn{:}} \quad \mathrm{R{-}X} \longrightarrow \mathrm{Sn^{\dot{+}}} \quad + \quad \mathrm{R^{\bullet}} \quad + \quad \mathrm{X^-}$$

$$\mathrm{Sn^{\dot{+}}} \quad + \quad \mathrm{X^-} \longrightarrow \mathrm{SnX^{\bullet}}$$

$$\mathrm{SnX^{\bullet}} \quad + \quad \mathrm{R^{\bullet}} \longrightarrow \mathrm{RSnX}$$

Subsequently, oxidative addition (insertion into the carbon-halogen bond of a second mole of the alkylhalide) occurs to form the diorganotin dihalide.



Under certain circumstances, direct reaction may occur in the absence of a catalyst. Sisido and coworkers[21] found, somewhat surprisingly, that the reaction between benzyl chloride and tin powder, in an aqueous medium at 100°C, resulted in an excellent yield of tribenzyltin chloride (2):-

$$3\ C_6H_5CH_2Cl + 2Sn \xrightarrow[H_2O]{\text{reflux}} \underset{(2)}{(C_6H_5CH_2)_3SnCl} + SnCl_2$$

94% yield

However, in a non-polar solvent the more usual product of direct synthesis, dibenzyltindichloride (3) was obtained:-

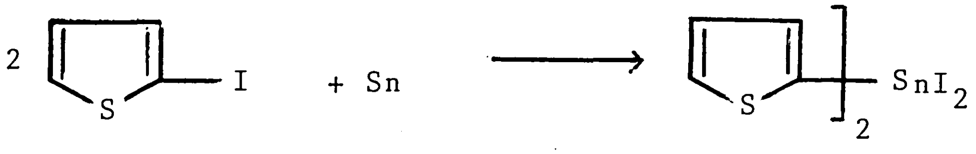
$$2C_6H_5CH_2Cl + Sn \xrightarrow[\text{reflux}]{\textbf{Toluene}} \underset{(3)}{(C_6H_5CH_2)_2SnCl_2}$$

88% yield

It is now generally accepted that, in the aqueous reaction, dibenzyltin dichloride is formed initially and then proceeds to react with tin powder to give the triorganotin halide[22,23]

i.e. $3\ (C_6H_5CH_2)_2SnCl_2 + Sn \xrightarrow{H_2O} 2\ (C_6H_5CH_2)_3SnCl + 2SnCl_2$

This type of reaction has also proved useful in the preparation of heteroaryltin derivatives (see also section 1.3). Gopinathan and coworkers[24] prepared di(2-thienyl)tin diiodide, (4) from 2-iodothiophen and tin metal in the presence of a catalytic amount of pyridine hydrochloride, and this product was subsequently characterised by the formation of chelated tin (IV) compounds,(see chapter 1, p.27)



(4)

Diorganotin dihalides may also be prepared from tin (II) halides by reaction with a suitable organometallic reagent[25]

e.g. $Ph_2Hg + SnCl_2 \longrightarrow Ph_2SnCl_2 + Hg$

Direct alkylation of tin (IV) halides to give organotin halides is possible with many organometallic reagents such as Grignard or organolithium compounds but, even when molar ratios are carefully controlled, a mixture of the three possible halides, $R_nSnX_{4-n}$, (n=1-3) usually results. Thus the preferred synthetic route is usually via the symmetrical tetraorganotin, $R_4Sn$.

However, if the organic group is fairly bulky, partial substitution of the tin (IV) halide may then occur to give good yields of the organotin halide. For example, the reaction of three moles of cyclohexylmagnesium chloride with one mole of tin (IV) chloride to form tricyclohexyltin chloride (5), is possible[26].

$$3CyMgCl + SnCl_4 \longrightarrow \underset{(5)}{Cy_3SnCl} + 3\,MgCl_2$$

Selective disubstitution of tin (IV) halides has also been achieved with certain reagents[27]

$$2\,Bu^tMgCl + SnCl_4 \longrightarrow Bu^t{}_2SnCl_2 + 2MgCl_2$$

The use of organocopper compounds in organic synthesis has increased greatly in recent years.

Koten <u>et al</u>[28] have achieved the synthesis of triaryltin halides by a single step process involving arylcopper(I) compounds.

$$PhLi + CuBr \xrightarrow{-LiBr} PhCu \xrightarrow[-\ CuCl]{\frac{1}{3}\ SnCl_4} \tfrac{1}{3}\,Ph_3SnCl$$

In a recent preliminary communication, Chandrasekaran *et al*[29] outline a novel synthetic route to diorganotin dihalides. The reaction involves treatment of $(acac)_2SnX_2$, (where acac = pentane -2,4 - dionate anion) with an appropriate Grignard reagent:-

$$2\ PhMgBr + (acac)_2\ SnBr_2 \longrightarrow Ph_2SnBr_2 + 2\ acacMgBr$$

(60% yield)

The authors claim a single product in contrast to the $R_nSnX_{(4-n)}$ mixture obtained when reacting tin (IV) chloride with the same Grignard reagent in a 1:2 molar ratio.

Oxidative addition reactions of tin(II) bis(acetylacetonate) with organic halides have also provided a route to novel monoorganotin (IV) bis(acetylacetonate) halides[30]. The reaction is based on that of tin (II) halides with organic halides to form monoorganotin trihalides, the interest in oxidative addition to tin (II) compounds arising from their possible position as intermediates in the direct synthesis of diorganotin dihalides from the organic halide and tin metal. Thus when tin (II) acetylacetonate is heated with benzyl bromide, the monoorganotin halide (6) is formed.

$$Sn(acac)_2 + C_6H_5CH_2Br \longrightarrow \underset{(6)}{C_6H_5CH_2Sn(acac)_2Br}$$

As suggested by Scheme 2.1, organotin chlorides are important starting materials for the synthesis of other organotin halides by displacement of the chloride ion using a suitable metal halide[1].

$$R_nSnCl_{(4-n)} + (4-n)\,MX \longrightarrow R_nSnX_{(4-n)} + (4-n)MCl$$

($X$ = F, Br or I; M=K, Na, $NH_4$, etc.)

By alkaline hydrolysis, organotin halides are converted into the corresponding organotin hydroxide or organotin oxide. These latter compounds can then be made to react with a suitable halogenating agent to yield the desired organotin halide. The reaction is of use in instances where organotin halides cannot be obtained in a pure form or good yields by other more classical methods.

Organotin halides may be prepared from the corresponding hydrides by cleavage of tin-hydrogen bonds using halogens, hydrogen halides or organic halides. However, this method would appear to be unsuitable for preparation of aryltin halides as tin-carbon bond cleavage may occur preferentially[31]. Thus when triphenylstannane is treated with hydrogen bromide, diphenylbromostannane (7) is formed.

$$Ph_3SnH + HBr \xrightarrow{-78^{\circ}\,C} \underset{(7)}{Ph_2SnHBr} + PhH.$$

The tin-tin linkages of hexaorganodistannanes or polymeric diorganostannanes are also cleaved by halogens to produce good yields of the corresponding halides. However, these reactions are only of importance when very pure tri- and diorganotin halides are required as the starting materials are usually prepared from the organotin halides in the first instance[32].

$$R_3SnSnR_3 \quad + \quad X_2 \longrightarrow 2R_3SnX$$

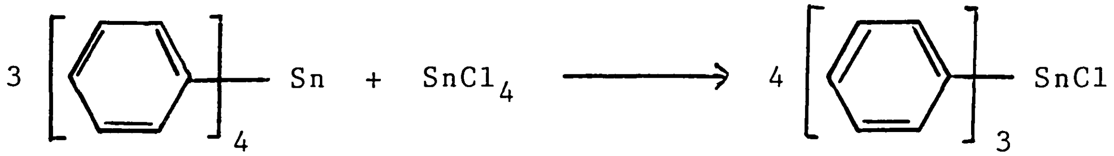
$$(R_2Sn)n \quad + \quad nX_2 \longrightarrow nR_2SnX_2$$

## 2.2. Attempted Synthesis and Characterisation of Heteroaryltin Halides

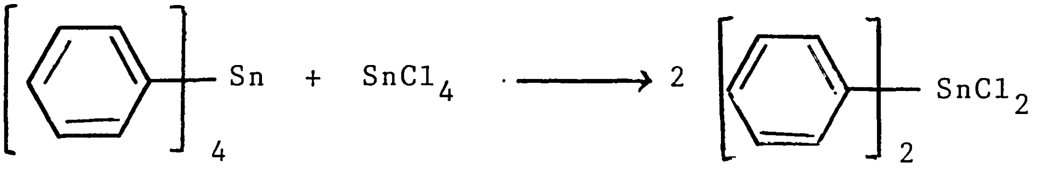
As the most readily accessible starting materials, pure samples of tetra (2-thienyl)tin and tetra(2-furyl) tin were prepared as previously described (see section 1.3) from reactions between the appropriate 2-heteroaryllithium reagent and tin(IV) chloride. Melting point data were consistent with those published in the literature and mass spectra were also confirmatory. The fragmentation patterns for tetraorganotins under electron impact can normally be easily related to the stable (IV and II) and unfavourable (III and I) valence states of tin[33,34]. The molecular ion is usually relatively weak due to the instability of the abnormal Sn(V) state, which has been assumed to arise from the removal, from tin, of an inner shell electron[35,36]. The base peak is often the Sn(IV) species, $R_3Sn^+$, whereas the diorganotin cation, $R_2Sn^+$, is normally of low abundance and the divalent component $RSn^+$, of relatively high intensity. In tetra(2-thienyl)tin and tetra (2-furyl)tin, the molecular ion is well defined but can only be considered as having moderate intensity when compared with the major tin-containing fragments, $Ar_3Sn^+$ and $ArSn^+$. The trivalent species, $Ar_2Sn^+$, is of very low abundance. Additionally there is some evidence of furyl ring degradation in the spectrum of tetra(2-furyl)tin with the presence of the tin isotopic splitting at m/e ($ArSn^+$ - 28) which may correspond to expulsion of carbon monoxide from the furyl ring[37].

## Initial Reactions with Tin (IV) Halides

With a view to preparing the tri-and diheteroaryltin halides, the first synthetic routes considered involved redistribution reactions between the tetraorganotin compounds and tin (IV) chloride. These reactions necessitated an inert atmosphere due to the ready hydrolysis of tin (IV) chloride but required no solvent. Prior to the attempted preparation of any heteroaryltin halides by this method, pilot syntheses of the well known phenyltin chlorides were carried out. When tetraphenyltin and tin (IV) chloride were heated together, at elevated temperatures, for several hours in a 3:1 molar ratio, thin layer chromatography was indicative of the major product having properties consistent with the desired triphenyltin chloride (8). Melting point data and mass spectra confirmed the recrystallised product to be the triorganotin halide. Under similar conditions but in equimolar quantities the same reagents produced a low melting solid which was subsequently found to be diphenyltin dichloride (9) upon examination of mass spectral, t.l.c. and melting point data.

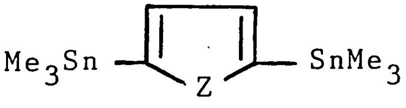


(8)



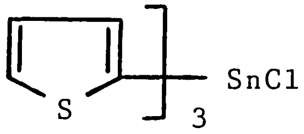
(9)

The reaction between three moles of tetra(2-thienyl) tin and one mole of tin (IV) chloride yielded, after cooling, a grey crystalline material. TLC indicated the product to be of intermediate polarity with respect to triphenyltin chloride and diphenyltin dichloride, although streaking on the t.l.c. plate was evident and this may be consistent with decomposition of the product on contact with an acidic medium. Indeed Seitz and co-workers[38] prepared some 2,5-bis (trimethylstannyl) derivatives (10) of thiophen and furan for which attempted analysis by t.l.c. resulted in extensive protodestannylation. An attempted recrystallisation of the suspected tri(2-thienyl)tin chloride (11) from isopropyl alcohol resulted only in the formation of a white insoluble high-melting solid. Mössbauer studies showed the tin-containing species to be tin (IV) oxide, presumably in association with some organic material. Similar problems were encountered with the 2-furyl analogue.



Z = O or S

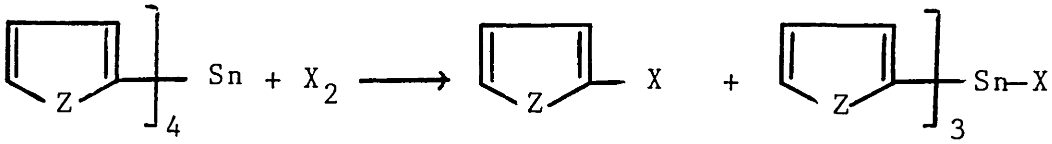
(10)



(11)

The use of tin (IV) bromide and tin (IV) iodide in these reactions proved more useful in that molar quantities could be controlled more rigidly than with tin (IV) chloride which hydrolyses rapidly on exposure to air. In all instances, redistribution reactions produced the required di- and triheteroaryltin halides, from the appropriate molar quantities of tetraheteroaryltin and tin (IV) halide, as the major product. However, traces of the alternative products of redistribution were also detected in these reaction mixtures by spectroscopic and Mössbauer techniques. Recrystallisation attempts resulted only in decomposition to tin (IV) oxide and vacuum distillation provided a more complicated mixture than the original crude material presumably as a result of further redistribution/disproportionation reactions occurring in the vapour phase. Such redistribution reactions therefore afford routes to the desired compounds, but the main problem would seem to be the isolation and characterisation of the products.

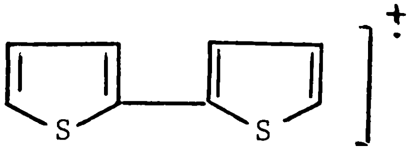
Reactions with Halogens



Tetra(2-thienyl)tin and tetra(2-furyl)tin were both treated with equimolar quantities of iodine and bromine, respectively. The reaction between tetra-(2-thienyl)tin and iodine, in an inert nitrogen atmosphere with chloroform as the solvent, produced, on evaporation, a crystalline solid with encouraging t.l.c. properties although there appeared to be a small amount of tetra(2-thienyl)tin remaining. Once more the inherent instability of the suspected triorganotin halide excluded further purification of this material. Reactions of tetra(2-furyl)tin with both bromine and iodine were less promising with t.l.c. inferring the apparent production of either mono-organo- or inorganic tin species and a large proportion of unreacted tetra(2-furyl)tin, even though the rate of halogen addition was carefully controlled. Thus reactions between halogens and these particular tetra-heteroaryltin compounds in solution appear to be less suitable for the preparation of triheteroaryltin halides than the redistribution reactions with tin (IV) halides, and may also provide the first indication that the desired products are unstable in solution with respect to disproportionation, e.g. according to $2R_3SnCl \longrightarrow R_4Sn + R_2SnCl_2$

This yields a more complex mixture of redistribution products, such as is observed on attempted purification by vacuum distillation, with an apparent tendency for reactions to proceed towards the formation of the stable tetraorganotin species.

However, when a chloroform solution of iodine monochloride was added dropwise to tetra(2-thienyl)tin, also in chloroform, an initial pink colouration quickly dispersed and a white solid gradually precipitated out of the solution. Extraction of this solid with dry hexane produced a solution from which two or three small, "brick-like", transparent crystals were obtained. T.l.c. was consistent with a pure triorganotin species and the mass spectrum (fig.2.2.1.) provided strong evidence for these crystals being tri(2-thienyl)tin chloride (11). The most abundant tin containing fragment is due to the tin (II) species $Sn^+Cl$, reflecting the strength of the tin-halogen bond, but the (2-thienyl)$Sn^+$ fragment is also prominent reflecting the stability of divalent tin. Fragments due to the other stable valence state of tin, Sn(IV), are also prominent, particularly the $(2\text{-thienyl})_2 Sn^+Cl$ component. The molecular ion for this compound is also easily identifiable. The major non-tin-containing signal appears at m/e 166, and may possibly be due to the dithienyl ion (12). The mass spectra of a number of bithienyls have been recorded[37].



(12)

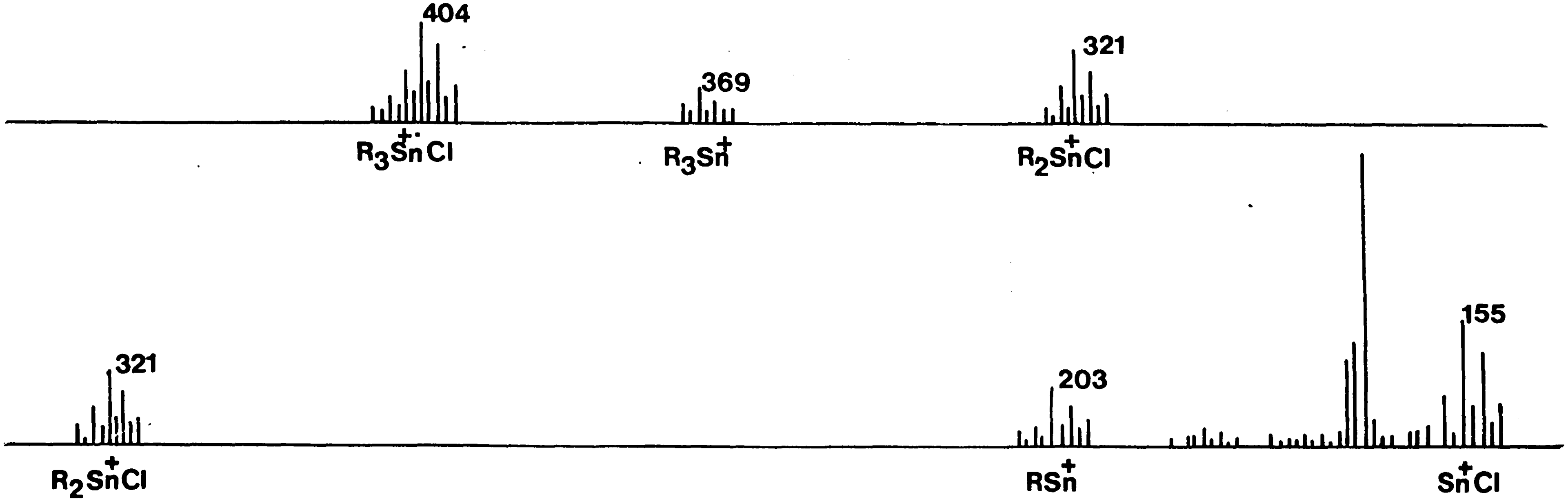
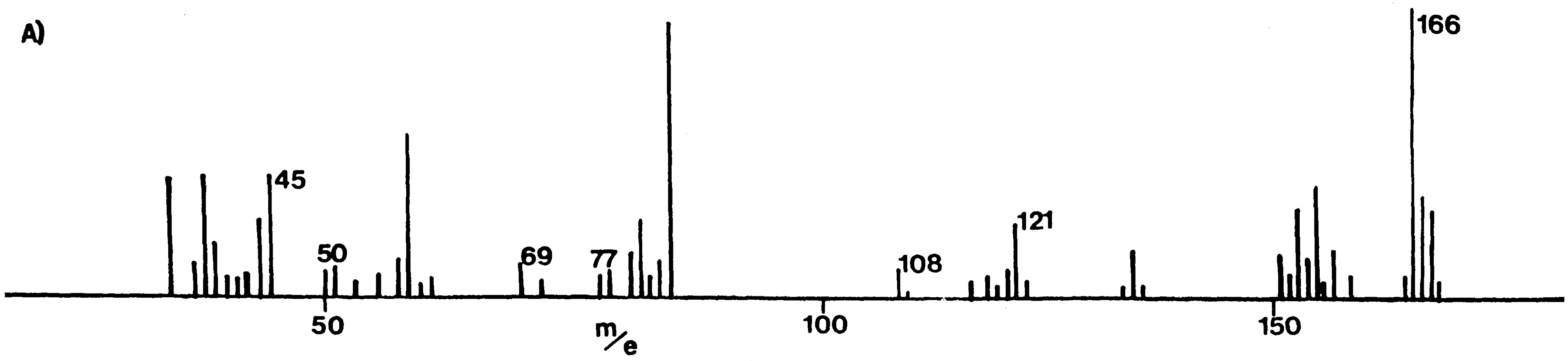


Fig. 2.2.1 Mass Spectrum of Tri-(2-Thienyl)Tin Chloride

Apart from small differences in relative ion intensities, the spectra of 2,2' - dithienyl and 2,3' - dithienyl are similar to that of the 3,3' -isomer [39,40] and it is possible that all three fragment <u>via</u> a common isomerised molecular ion. The mass spectrum of 3,3' - dithienyl does in fact exhibit, to some extent, the same m/e pattern as tri(2-thienyl)tin chloride and it is therefore not unreasonable to suggest that the fragment at m/e 166 may arise from $(\text{dithienyl})^{+\cdot}$ (Fig. 2.2.2.) Unfortunately, these transparent crystals did not remain stable for a period of time sufficient to gain further analytical data and became opaque and insoluble after a short while. This proved to be an important observation with respect to the air and/or water instability of such compounds. The major product of this reaction has not been positively identified, the high insolubility suggesting a possible polymeric structure and precluding thorough investigation by n.m.r. techniques. Attempts to follow the reaction course by $^{119}Sn$ n.m.r. spectroscopy have revealed a steady decline in the amount of tetra(2-thienyl)tin and the appearance of a relatively weak signal at $\delta$ = 65 ppm (relative to $Me_4Sn$) consistent with the formation of tri(2-thienyl)tin chloride (see later studies). However, once more the major product precipitated from solution in the sample tube and no significant chemical shift was observed for this species. However a small, otherwise unaccountable, signal does appear at $\delta$ = -50ppm and this may arise from the limited



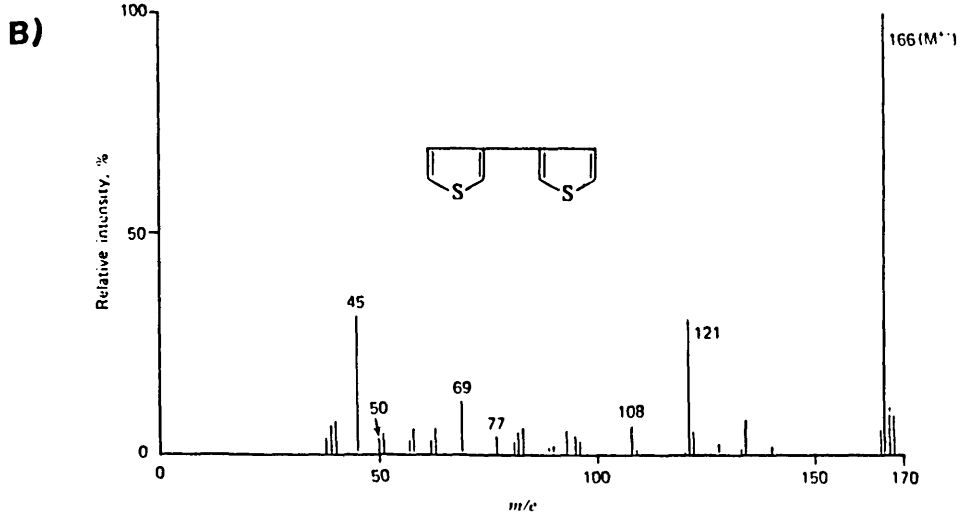


Fig. 2.2.2

Mass Spectra of

A) Tri-(2-thienyl)tin Chloride and

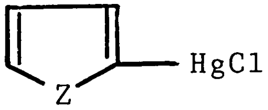
B) 3,3'-Dithienyl.

solubility of the unknown product.

The same reaction between tetraphenyltin and iodine monochloride was much less vigorous, the initial pink colouration fading much more slowly. Under similar reaction conditions to those employed for the 2-thienyl analogue, the reaction was found to be incomplete, a considerable proportion of unreacted tetraphenyltin being recovered. However some triphenyltin chloride was isolated from the reaction mixture and its mass spectrum found to be similar to that of the assumed tri(2-thienyl)tin chloride with the exception of the observation of a reduced intensity molecular ion for the more stable phenyl-containing compound.

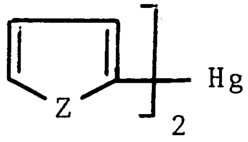
Reactions with mercury (II) compounds

Equimolar quantities of mercury (II) chloride and tetraphenyltin dissolved in methanol and tetrahydrofuran respectively, were stirred together in the dark without heating. On hydrolysis with aqueous salt solution, a white solid persisted and was subsequently filtered off. The filtrate was extracted into chloroform and evaporation left a second solid identified as triphenyltin chloride. Melting point data indicated that the first, less soluble, solid was phenylmercury (II) chloride. When tetra(2-furyl)tin and tetra(2-thienyl)tin were allowed to react with mercury (II) chloride under the same conditions but with omission of the aqueous work-up, only the 2-furyl- and 2-thienylmercury(II) chlorides (13) could be isolated.



Z = O or S

(13)



Z = O or S

(14)

One possible reason for the apparent decomposition of the expected triorganotin compounds was the use of a protic solvent, methanol, to dissolve the mercury(II) chloride. The same experiments were repeated using dimethyl formamide (DMF), a dipolar aprotic solvent, in a single solvent system. Under these conditions a DMF insoluble material was isolated from the reaction between tetra (2-thienyl)tin and mercury(II) chloride and subsequently identified as di(2-thienyl) mercury(II) (14,Z=S). The solid residue from the DMF-soluble fraction gave rise to a complicated mass spectrum indicating the presence of a mixture of thienyltin chlorides, including a significant amount of di(2-thienyl)tin dichloride. T.l.c. was also consistent with the formation of di(2-thienyl) mercury and a mixture of more polar organotin chlorides. The same reaction with tetra(2-furyl)tin produced an orange/brown oil upon rotary evaporation of the DMF. Subsequent analysis revealed the presence of di(2-furyl) mercury (14,X=O) and a number of furyltin chlorides. Thus these observations confirm that protic solvents would appear to promote the cleavage of tin - carbon bonds in heteroaryltin chlorides of this type, an attempted recrystallisation of tri-(2-thienyl) tin chloride from isopropyl alcohol already having been observed to cause decomposition to tin(IV) oxide. However, DMF would appear to be too reactive a medium to control the reaction to a single substitution at tin as indicated by the formation of di(heteroaryl) mercury compounds. Using tetrahydrofuran as the sole solvent the reactions between mercury(II) chloride and the tetra (2-heteroaryl)tin compounds were repeated. The expected 2-furyl - and 2-thienylmercury (II) chlorides were obtained; however, the triorganotin chlorides remained illusive as single isolable products. Similar problems were encountered with parallel reactions employing mercury (II) acetate.

## Direct Synthesis

As described in the literature[24] the direct synthesis of di(2-thienyl)tin diiodide (4) has been achieved from the reaction of tin powder with 2-iodothiophen in the presence of a catalytic amount of pyridine hydrochloride. In the present study, the product was purified by vacuum distillation to yield a pale yellow oily liquid. However in addition to this oil, a small quantity of crystalline material was also obtained. This solid was subsequently identified as tetra(2-thienyl)tin from t.l.c. evidence and the Mössbauer spectrum of the distillate which exhibited a quadrupole doublet for the diorganotin species together with a singlet arising from the symmetrical tetraorganostannane (Fig. 2.2.3.). The concurrent formation of tetra (2-thienyl)tin had not been previously reported and may have resulted from the redistribution of

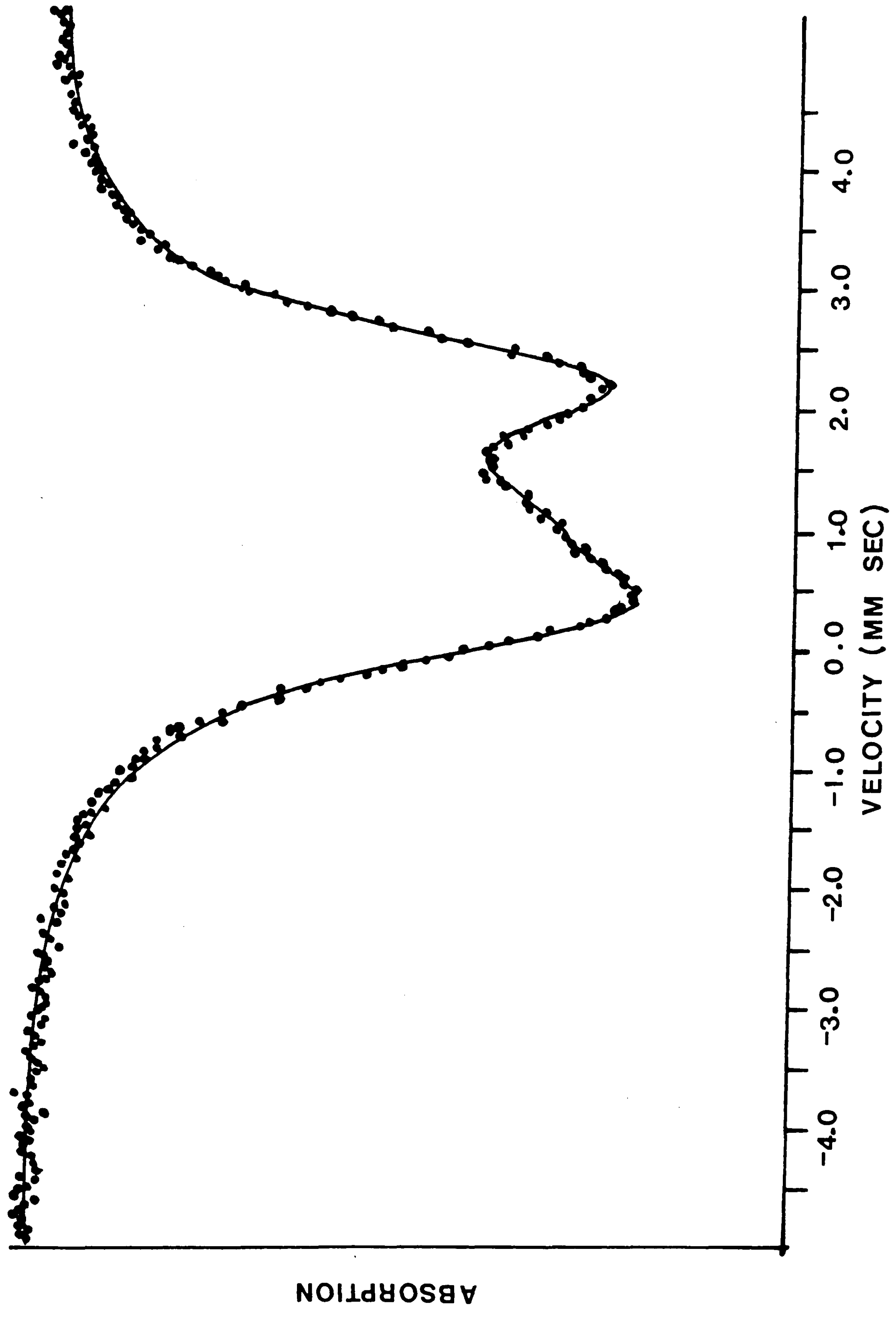
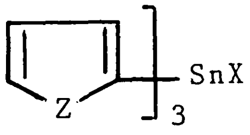


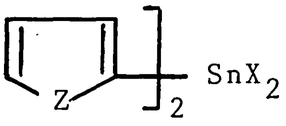
Fig. 2.2.3. Mössbauer spectrum of the distillate from the reaction between iodothiophene and tin metal.

di(2-thienyl)tin diiodide in the vapour phase to yield the tetraorganostannane and tin (IV) iodide which undoubtedly accounted for the sublimation of an orange/red solid on the walls of the distillation apparatus. This reaction thus provides further evidence of the unsuitability of vacuum distillation for obtaining pure organotin halide products incorporating heteroaryl substituents of this type.

The above preliminary studies therefore indicate that the preparation of tri- and di(2-heteroaryl)tin halides is possible by redistribution and other reactions and that some of the diorganotin dihalides may also be obtained by direct methods. However, purification, and especially separation from other reaction products, appeared to be a major problem.



(15)



(16)

Z = O or S

X = Cl,Br or I

In subsequent work, the triorganotin halides (15) were all prepared by redistribution reactions of tetra-(2-heteroaryl)stannanes and the appropriate tin (IV) halide. Without exception, these compounds have been found to be unstable, readily decomposing on attempted distillation or recrystallisation, or even on standing at room temperature, traces of moisture promoting their decomposition to tin (IV) oxide. The corresponding diorganotin dihalides (16) have also been obtained by redistribution reactions, (with the exception of di(2-thienyl)tin diiodide which was prepared by direct synthesis), and were found to be similarly unstable. The inherent instability of these compounds together with difficulties encountered in their attempted purification have proved a considerable handicap with respect to their characterisation. However, it has been possible to obtain Mössbauer spectra of all of these compounds immediately following their formation. The inert atmosphere and low temperatures employed in this technique ensure minimal decomposition of the sample. Additionally, impurities of up to 5% by weight have very little influence on the overall spectrum.

## Mössbauer Data

The Mössbauer data for the 2-furyl- and 2-thienyl-tin halides are given in Table 2.2.1. The Mossbauer spectra of tri(2-furyl)tin chloride and di(2-thienyl)tin dibromide are displayed in figures 2.2.4. and 2.2.5. respectively. All the spectra consist of a quadrupole-split doublet, the magnitude of the splitting indicating that the tin atom is four coordinate and that there is no evidence of intermolecular association leading to an increase in the co-ordination number at tin. This would appear to be the case for both the tri- and di-organotin halides. The Mossbauer data obtained exhibit several interesting

## TABLE 2.2.1

## Mössbauer Data for 2-Furyl- and 2-Thienyl Tin Halides

| | Isomer Shift,[a] (mm/s ± 0.02) | Quadrupole Splitting, (mm/s ± 0.02) |
|---|---|---|
| (i) $R_3SnX$ | | |
| $(2\text{-}C_4H_3O)_3SnCl$ | 1.14 | 2.14 |
| $(2\text{-}C_4H_3O)_3SnBr$ | 1.17 | 2.19 |
| $(2\text{-}C_4H_3O)_3SnI$ | 1.23 | 1.84 |
| $(2\text{-}C_4H_3S)_3SnCl$ | 1.13 | 1.99 |
| $(2\text{-}C_4H_3S)_3SnBr$ | 1.18 | 1.99 |
| $(2\text{-}C_4H_3S)_3SnI$ | 1.20 | 1.77 |
| (ii) $R_2SnX_2$ | | |
| $(2\text{-}C_4H_3O)_2SnCl_2$ | 1.10 | 2.09 |
| $(2\text{-}C_4H_3O)_2SnBr_2$ | 1.17 | 1.80 |
| $(2\text{-}C_4H_3O)_2SnI_2$ | 1.34 | 1.42 |
| $(2\text{-}C_4H_3S)_2SnCl_2$ | 1.14 | 2.06 |
| $(2\text{-}C_4H_3S)_2SnBr_2$ | 1.21 | 1.96 |
| $(2\text{-}C_4H_3S)_2SnI_2$ | 1.26 | 1.84 |
| $(2\text{-}C_4H_3O)_2SnBr_2$.bipy | 0.98 | 2.85 |
| $(2\text{-}C_4H_3S)_2SnCl_2$.bipy | 0.75 | 1.69 |

a Relative to $BaSnO_3$

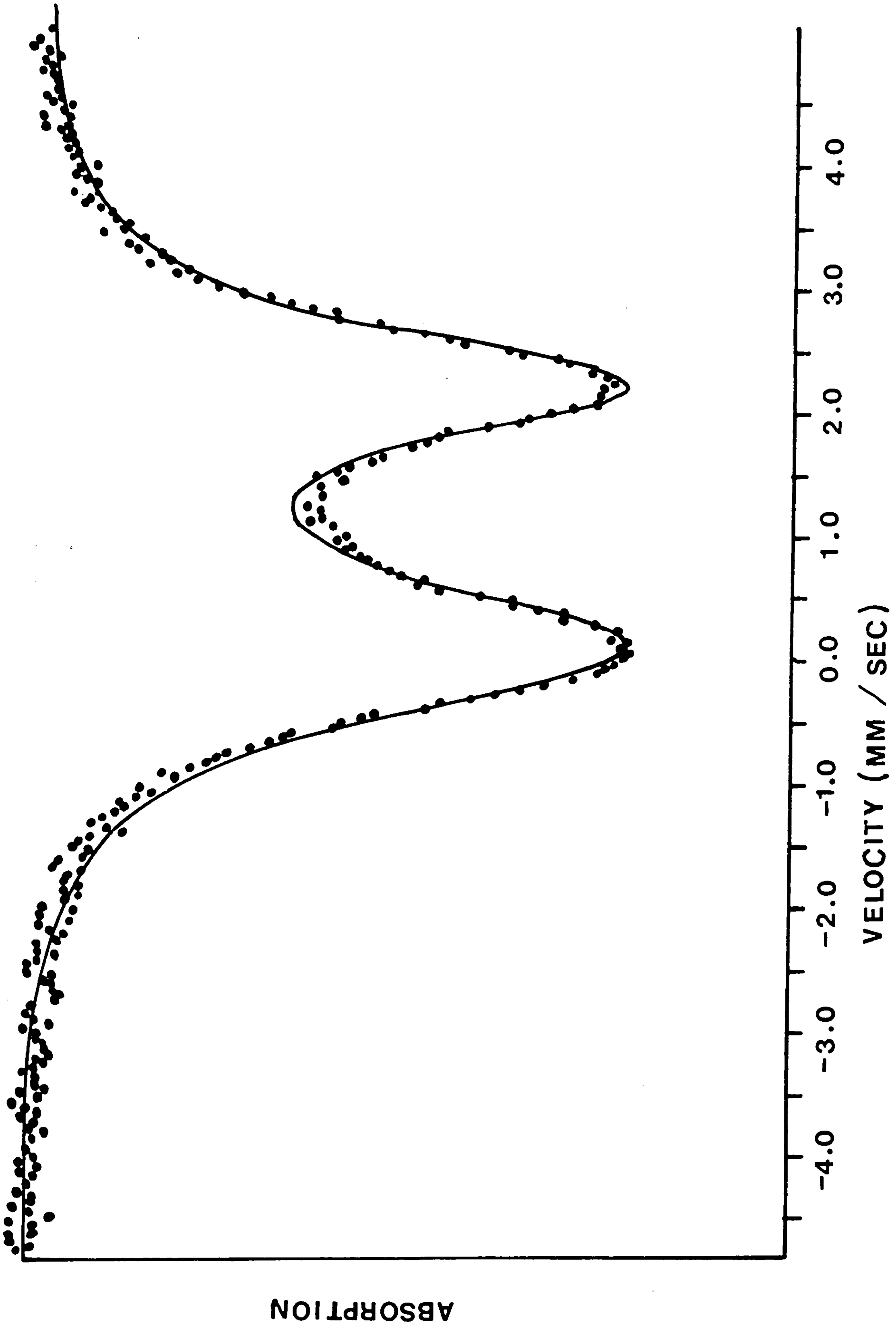


Fig. 2.2.4.

Mõssbauer spectrum of Tri(2-furyl)tin chloride

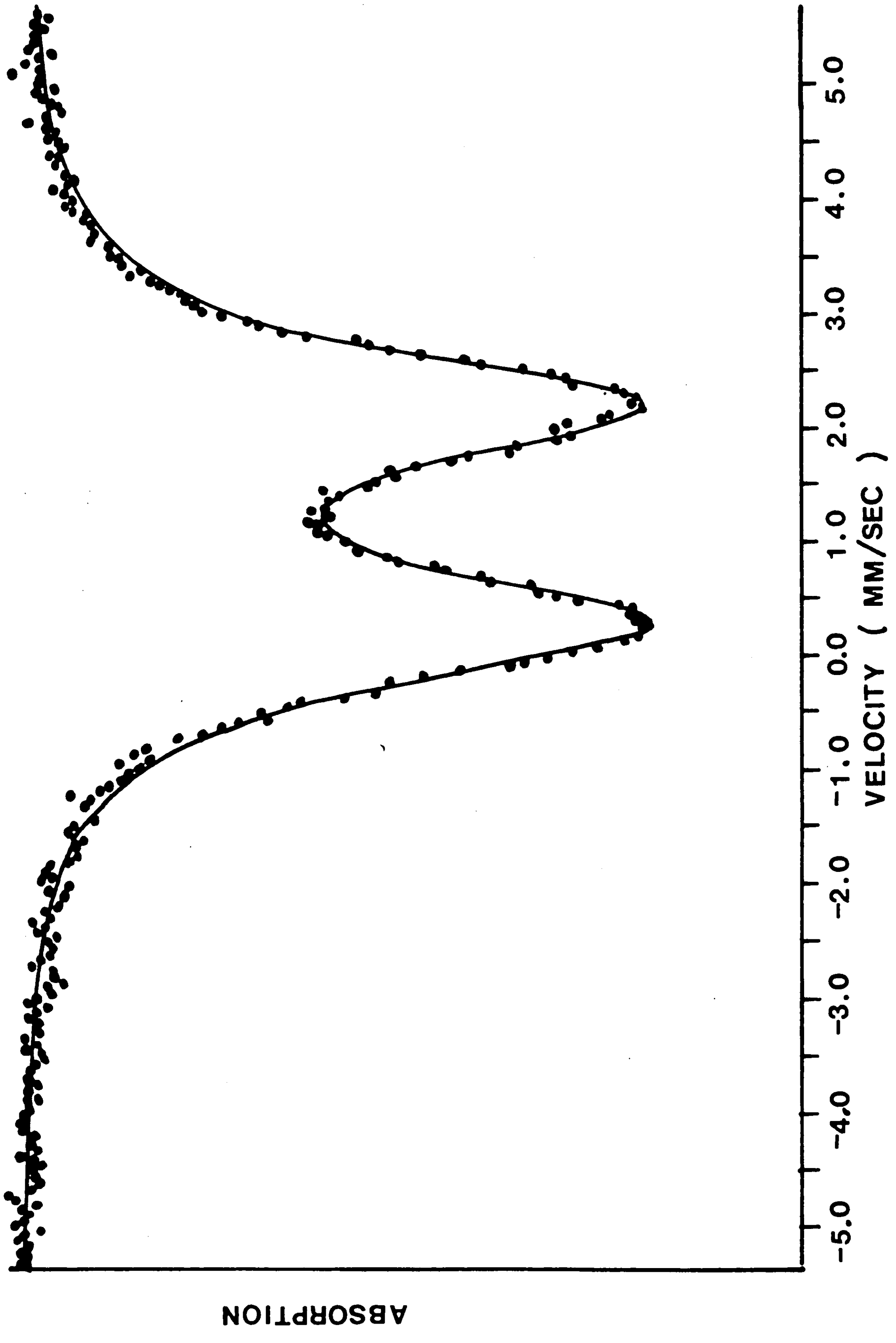


Fig. 2.2.5.

Mössbauer spectrum of Di(2-thienyl)tin dibromide trends which are largely consistent with those previously observed for the much studied phenyl analogues (Table 2.2.2.) As the halogen is changed from chlorine to bromine to iodine there is an increase in the isomer shift. This is due to a lowering in electronegativity of the substituent halogen which results in an increase in *s*-electron density at the tin atom. As expected, the magnitude of this effect is increased for the diorganotin dihalides relative to the monohalo species.

While the isomer shift increases with decreasing electronegativity of the halogen, the reverse is true of the quadrupole splitting data. This is consistent with a decrease in the asymmetry of the electric field gradient at the Mössbauer nucleus as the electronegativity of the halogen decreases.

TABLE 2.2.2.

Mössbauer Data for Triphenyltin Halides and Diphenyltin Dihalides

| | Isomer Shift,[a] (mm/s ± 0.02 | Quadrupole Splitting, (mm/s ± 0.02) |
|---|---|---|
| $Ph_3SnCl$ | 1.37 | 2.45 Ref (41) |
| $Ph_3SnBr$ | 1.37 | 2.46 |
| $Ph_3SnI$ | 1.41 | 2.05 Ref (42) |
| $Ph_2SnCl_2$ | 1.34 | 2.89 Ref (42) |
| $Ph_2SnBr_2$ | 1.43 | 2.54 Ref (43) |
| $Ph_2SnI_2$ | 1.51 | 2.38 Ref (43) |

a Relative to $BaSnO_3$

The Mössbauer parameters are also dependent on the electronegativity of the organic groups attached to tin. A comparison of isomer shifts for the 2-heteroaryltin halides with their phenyl analogues indicates that the electron-withdrawing properties of the organic groups attached to tin appear to increase in the order phenyl $<$ 2-thienyl $<$ 2-furyl. This is also apparent when comparing the Mössbauer isomer shifts of the associated tetraorganotin compounds (Table 2.2.3.) The quadrupole splitting parameter is also influenced; for example, the quadrupole splitting is smaller for tri(2-furyl)- and tri(thienyl)tin chloride than for the analogous phenyl derivative. This is presumably because the asymmetry introduced at the tin nucleus when an aryl group is replaced by an electronegative chlorine is notably less when heteroaryl substituents occupy the three remaining valencies.

In general, an increase in the number of halogens attached to tin, in the series $R_4Sn$, $R_3SnX$, $R_2SnX_2$ and $RSnX_3$, manifests itself in an increase in the isomer shift. This is contrary to the expected reduction in s-electron density at the tin atom due to the addition of electron-withdrawing groups. These results are consistent with suggestions that the use of isomer shift data to derive electronegativity values for various groups may be unreliable for mixed compounds. A qualitative understanding of the deviations observed has been offered on the basis

TABLE 2.2.3.

Mössbauer Data for Tetraheteroarylstannanes

| $Ar_4Sn$ | Isomer Shift,[a] (mm/s ± 0.02) |
|---|---|
| Ar = 2-Furyl | 1.06 |
| Ar = 2-Thienyl | 1.10 |
| Ar = 3-Thienyl | 1.16 |
| Ar = Phenyl | 1.26 |

[a] Relative to $BaSnO_3$

of substantial deviations from the simple $sp^3$ configuration of the tin when its surroundings are highly asymmetric. From assumptions made by analogy with Bent's rule[44] it has been shown that this change in hybridisation leads to an increase in the s density at the nucleus and thus a more positive isomer shift, the effect having been attributed to a different proportion of s and p character respectively, in the R-Sn and Sn - halogen bonds[45,46].

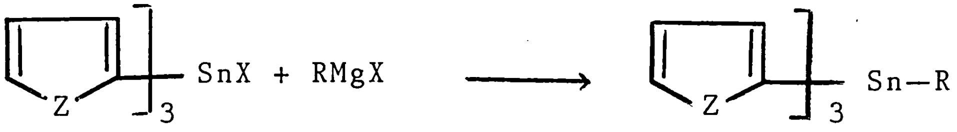
From the Mössbauer data presented, it would appear that the electron-withdrawing effect of the heteroatoms within these heteroaryl substituents is dominant and that there is little tendency for such " $\pi$ - excessive" heteroaromatic ring systems to be involved in interactions with the tin atom. A similar pattern is evident from studies of the reactivity of a wide range of similar derivatives of the main Group V elements[47].

The 2-furyl derivatives would appear to exhibit a higher degree of instability compared with their 2-thienyl analogues. This observation is again consistent with the strong $\sigma$ - inductive effect being predominant, especially for the 2-furyl substituents where the electronegative oxygen atom renders the tin-carbon bond particularly susceptible to electrophilic attack. The instability of the 2-heteroaryltin halides is presumably due to the ease with which they undergo protodestannylation reactions, a reflection of the tendency of furan and thiophen to undergo electrophilic substitution in the 2-position with great ease[48].

## Chemical Characterization

Although the above Mössbauer evidence was of considerable value in helping to characterise these highly unstable heteroaryltin halides, the need for a full chemical characterization was evident, particularly in view of the obvious short-comings of more traditional analytical methods when air-sensitive compounds are involved: Two methods, in particular, have been explored:-

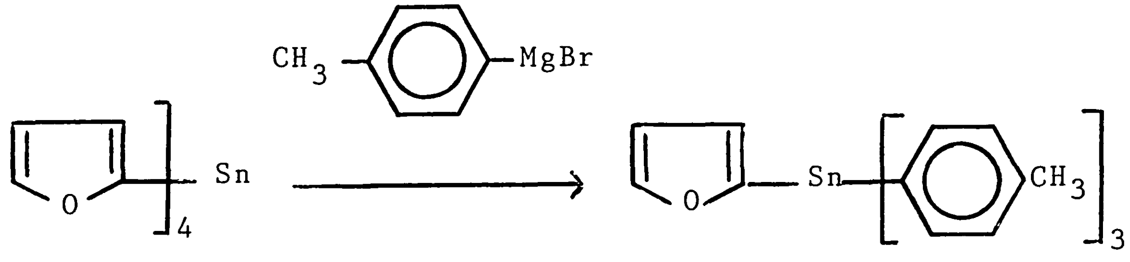
### (a) Reactions with Grignard or Organolithium Reagents



(17)

(18)

Reactions of this type were proposed as a means of converting the unstable, reactive heteroaryltin halides to stable mixed tetraorganotins[17,18]. The use of p-methoxy or p-tolyl organometallic reagents was thought appropriate as these groups would provide suitable $^1H$ nmr signals to monitor the extent of reaction and the purity of products. In all instances, when the di- and tri-(2-thienyl)- and (2-furyl)-tin halides were treated with a p-tolyl Grignard reagent in tetrahydrofuran (THF), a complex mixture of tetraorganotin compounds was revealed by thin layer chromatography and by mass spectra. Indeed Bobasinskaja and Kozechkow had previously encountered some difficulty when employing this method to characterise 2-thienyltin chlorides, achieving only poor yields of the expected mixed stannane[49]. The complexity of the product mixture was certainly in excess of that expected to arise as a consequence of the redistribution reaction employed in the preparation of the parent organotin halide. A number of reasons may contribute to the lack of success for this approach. The electron-withdrawing capabilities of the 2-heteroaryl substituent may be strong enough to render the tin-carbon bond susceptible to attack by the Grignard reagent, which would normally be present in excess. Indeed, a 'test' reaction between tetra(2-furyl)tin and an excess of the p-tolyl Grignard reagent produced tri(p-tolyl)(2-furyl)tin (19) as the major product.



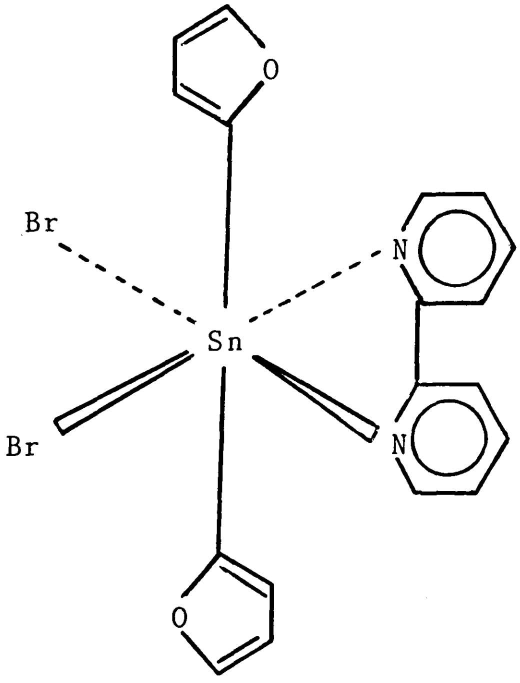
(19)

The significant $\sigma$- electron-withdrawing ability of the 2-furyl group would favour nucleophilic attack by the carbanionic reagent at tin with the possible formation of a pentacoordinate anionic intermediate of the type $(R_4SnR^1)^-$ from which the more stable 2-furyl anion would subsequently be ejected. In the case of the related 2-thienylstannanes, due to the smaller electron-withdrawing ability of the 2-thienyl group, this mode of reaction would be expected to be less favourable than for the 2-furyl analogue. Under similar conditions tetra(2-thienyl) tin reacted much less vigorously and a high proportion of unreacted tetra (2-thienyl)tin was recovered. However, thin layer chromatography did provide evidence of some tin-heteroaryl bond cleavage with the appearance a significantly less polar component. Thus the above problems associated with using this method as a chemical characterization for the 2-furyltin halides can be easily understood. A similar exchange reaction between tetra(2-thienyl)tin and the Grignard reagent may not be sufficient to account for the difficulties observed for the 2-thienyltin halides and other factors, such as the instability of these compounds with respect to disproportionation in solution, may be contributory.

### (b) Complex Formation

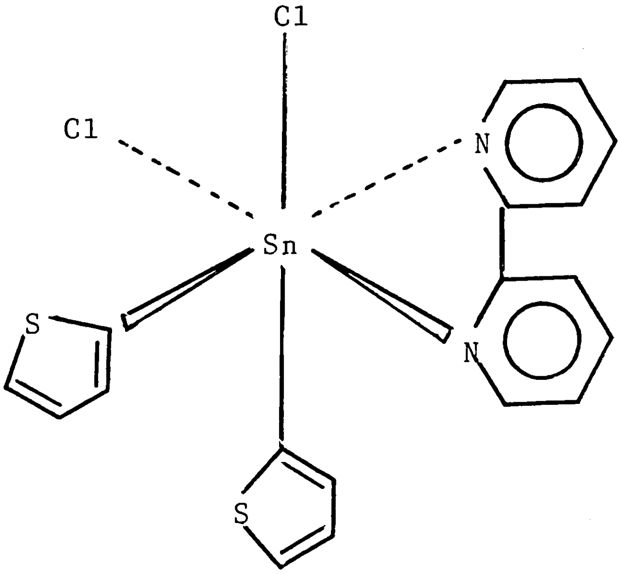
The chemical characterization of representative members of the 2-heteroaryltin halides has been attempted by the formation of stable adducts immediately following their preparation by redistribution reactions. Some degree of success has been achieved in characterising the di(2-heteroaryl)tin dihalides by complex formation with the bidentate ligands 2,2' - bipyridyl and *o* - phenanthroline.

Mössbauer data for the 2,2' - bipyridyl complexes of di(2-furyl)tin dibromide and di(2-thienyl)tin dichloride are included in Table 2.2.1. From the magnitude of the quadrupole splitting parameters, it would appear that the former has a distorted trans - octahedral structure (20), whereas the latter is likely to have cis-octahedral geometry (21) by analogy with Mössbauer data for related complexes[50] However, the quadrupole splitting parameter for the di(2-thienyl)tin dichloride - 2,2' - bipyridyl complex (1.69 mm/sec) is rather low for a cis - $R_2SnX_4$ type of system, and it is possible that this compound has a more complex structure in the solid state. Indeed, the Mossbauer spectrum exhibits some degree of asymmetry, although the line widths are consistent with the presence of only one tin site. It is of interest that the complex cis - diphenylbis(8-quinolato) -tin(IV) (22) also exhibits a quadrupole splitting of 1.69 mm $sec^{-1}$ [43].

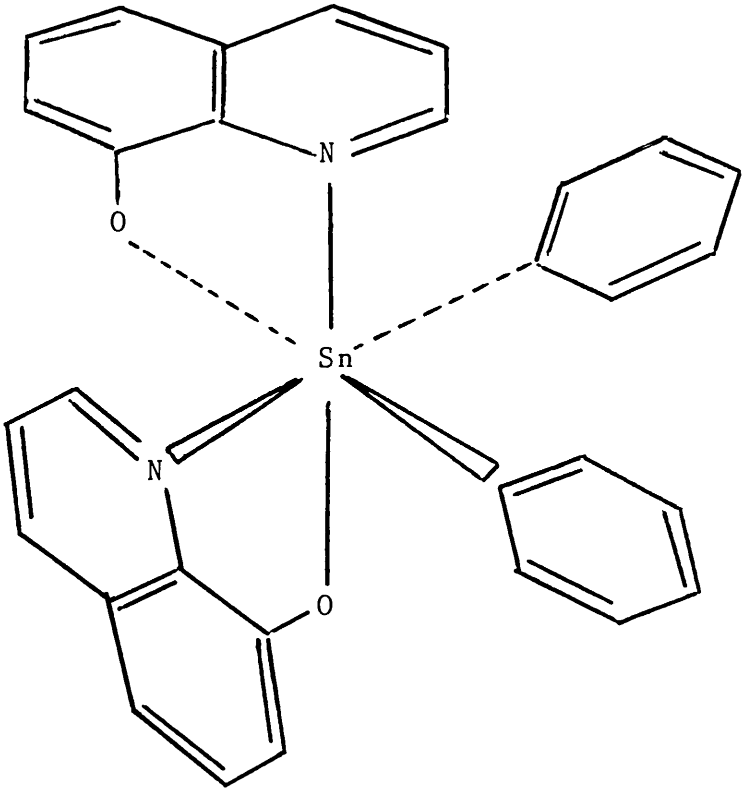


Trans - $R_2SnX_4$

(20)



(21) Cis - $R_2SnX_4$



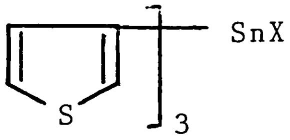
(22)

The use of triphenylphosphine oxide as a ligand for the complexation of the tri(2-heteroaryl)tin halides in toluene solution resulted in the formation of microcrystalline, toluene-insoluble, complexes. However although infrared and Mössbauer data were consistent with expected structures, microanalytical data revealed consistently high carbon figures, and it is likely that these adducts are mixtures of the complexes $R_3SnX.Ph_3PO$ and $[R_2SnX_2.\ (Ph_3PO)_2]$, the latter arising from the disproportionation of the initially formed triorganotin halide in solution and also, to a lesser extent, from the production of $R_2SnX_2$ as a minor product of the redistribution reaction employed in obtaining the parent triorganotin halide.

3- Heteroaryltin Derivatives

From the results obtained for, and the difficulties encountered with, the 2-heteroaryltin derivatives, the dominance of the $\sigma$- inductive effect within the 2-thienyl and 2-furyl substituents seemed apparent. Thus in the search for more stable heteroaryltin compounds, attention was directed towards the 3-thienyl and 3-furyl analogues, where, hopefully, the influence of the electronegative heteroatom within the ring would be considerably reduced.

Samples of tetra(3-thienyl)tin and tetra(3-furyl)tin were readily prepared, as described in the literature[52] by the reaction of 3-bromofuran or 3-bromothiophen with butyl lithium and then subsequent treatment of the 3-heteroaryl lithium reagent with tin (IV) chloride. In view of the relative electronegativities of sulphur and oxygen, the 3-thienyl systems were considered to be potentially more stable.



(23)

The tri(3-thienyl)tin halides (23, X=Cl,Br,I) were obtained by the redistribution reactions of tetra (3-thienyl)tin (3 mol) with the appropriate tin (IV) halide (1 mol). Whereas the reactions with tin (IV) bromide and chloride were conducted in the absence of a solvent at 150° C and were complete in a relatively short time, (ca 1-2 hr), the reaction with tin (IV) iodide proceeded more slowly. At the prevailing temperature, sublimation of tin (IV) iodide proved to be a problem, and hence the conversion was carried out under prolonged reflux in toluene solution. The resulting triorganotin halides were purified by recrystallisation and isolated as air-stable, analytically pure solids. Of the three halides, the iodide appeared to have the lowest thermal stability, there being some evidence of decomposition on recrystallisation.

The Mössbauer spectra of the solids (recorded at 80K) all show quadrupole-split doublets without line broadening; the spectrum of tri(3-thienyl)tin chloride is presented in Fig 2.2.6 and the Mössbauer parameters given in Table 2.2.4. As with the related phenyl- and 2-heteroaryltin halides, the quadrupole splitting parameters (and the Herber ratios[41]) are consistent with four coordination 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 interactions between the thienyl sulphur of one ring system and the tin atom of another molecule. X-ray studies have been carried out in order to clarify this point and are discussed in Chapter 3. A comparison of the Mössbauer data for these compounds with that already reported for the phenyl and 2-heteroaryl systems suggests that the 3-thienyl substituent is more electron-withdrawing than the phenyl group but less electron-withdrawing than the 2-heteroaryl moieties, and this offers some understanding of the increased stability of the 3-thienyltin halides over their 2-thienyl analogues.

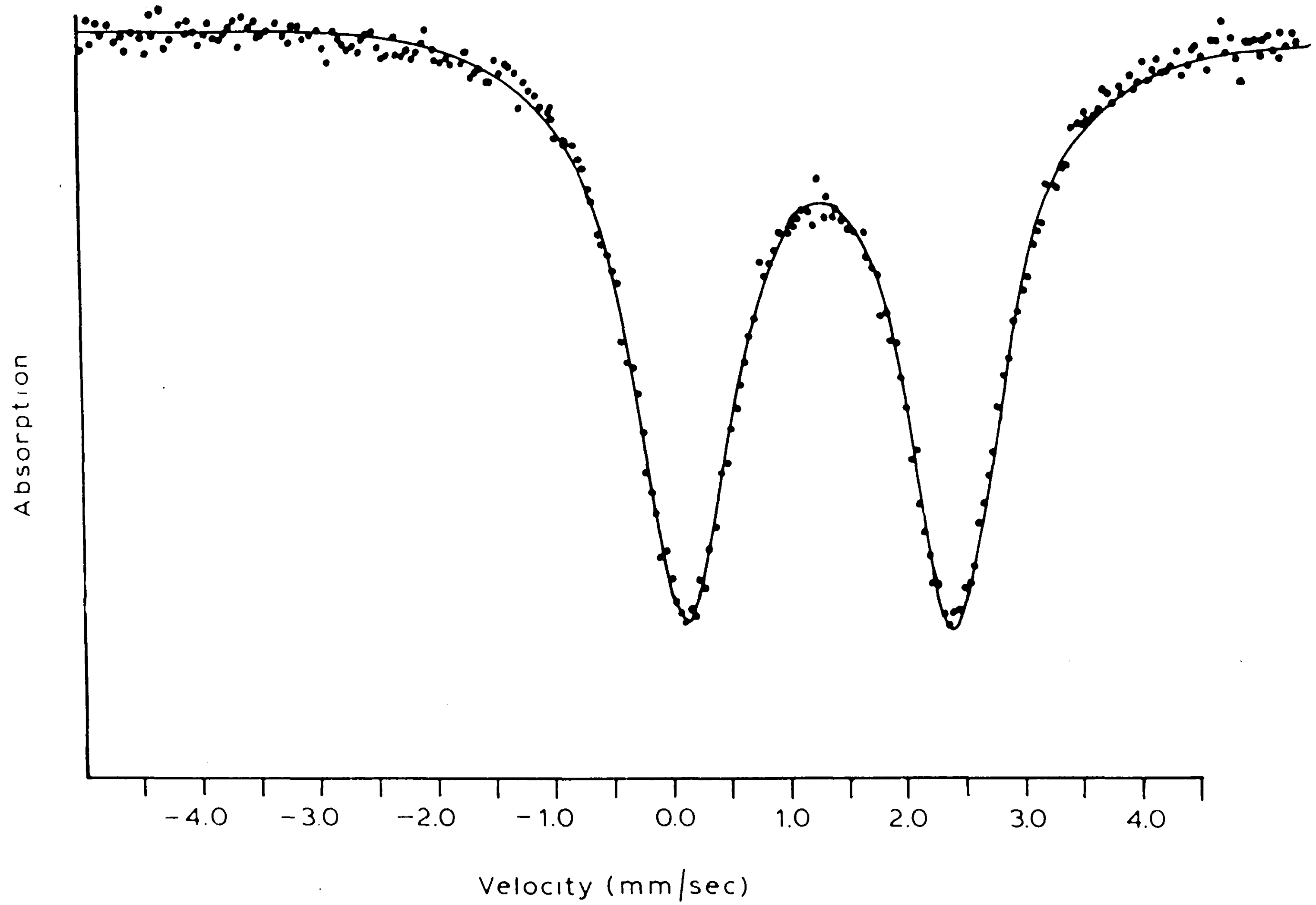


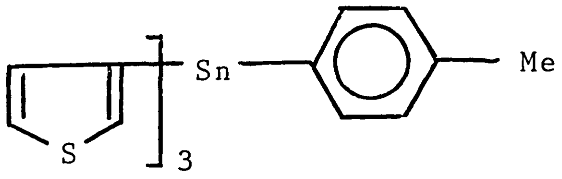
Fig. 2.2.6. Mössbauer spectrum of Tri(3-thienyl)tin chloride at 80 K.

TABLE 2.2.4.

Mössbauer Data for Tri-(3-Thienyl)tin Halides, Di-(3-Thienyl)tin Dihalides and Related Compounds

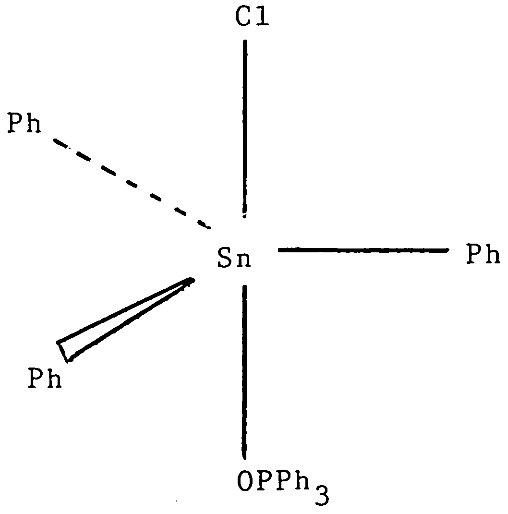
| | Isomer Shift,[a] (mm/s ± 0.02) | Quadrupole Splitting, (mm/s ± 0.02) |
|---|---|---|
| $(3\text{-}C_4H_3S)_3SnCl$ | 1.21 | 2.29 |
| $(3\text{-}C_4H_3S)_3SnBr$ | 1.25 | 2.08 |
| $(3\text{-}C_4H_3S)_3SnI$ | 1.29 | 2.02 |
| | | |
| $(3\text{-}C_4H_3S)_3SnCl.Ph_3PO$ | 1.18 | 3.08 |
| $(3\text{-}C_4H_3S)_3SnBr.Ph_3PO$ | 1.21 | 3.03 |
| | | |
| $(3\text{-}C_4H_3S)_2SnCl_2$ | 1.23 | 2.55 |
| $(3\text{-}C_4H_3S)_2SnBr_2$ | 1.30 | 2.30 |
| $(3\text{-}C_4H_3S)_2SnI_2$ | 1.29 | 2.01 |
| | | |
| $(3\text{-}C_4H_3S)_2SnCl_2$.bipy | 0.86 | 2.00 |
| $(3\text{-}C_4H_3S)_2SnBr_2$.bipy | 1.22 | 3.26 |

a Relative to $BaSnO_3$



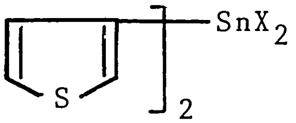
(24)

Treatment of tri(3-thienyl)tin chloride with an excess of p-tolylmagnesium bromide in ether gave the expected tri(3-thienyl) (p-tolyl)stannane (24). Both the chloride and the bromide readily formed insoluble 1:1 complexes on treatment with equimolar amounts of triphenylphosphine oxide in toluene solution. Coordination of the phosphoryl oxygen is indicated by a significant reduction in the P=O infrared stretching frequency, compared with that of free ligand, as observed for the related complex of triphenyltin chloride[53].



(25)

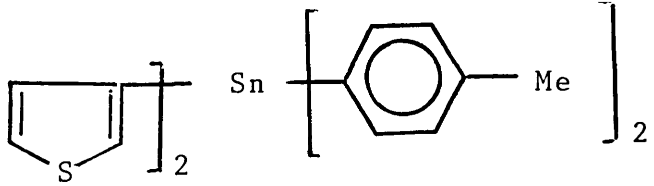
The Mössbauer parameters of the complexes (Table 2.2.4.) are very similar to those reported for the triphenylphosphine oxide complexes of triphenyltin chloride and bromide, for which trigonal bipyramidal structures (25) involving equatorial phenyl groups have been assumed on the basis of partial quadrupole splitting (p.q.s.) calculations[54,55]. In the present work, X-ray studies (Chapter 3) have confirmed that this type of structure is also found in the solid state for the triphenylphosphine oxide adduct of tri(3-thienyl)tin bromide.



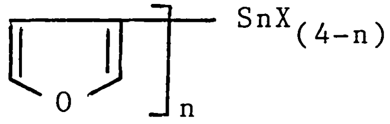
(26)

Di(3-thienyl)tin dichloride and dibromide (26,X=Cl or Br) have also been obtained by the redistribution reactions of equimolar quantities of tetra(3-thienyl)tin with tin (IV) halides. Both are liquids which resisted crystallisation at ambient temperatures. The related iodo derivative (26,X=I) was obtained by direct synthesis from metallic tin and 3-iodothiophen. As with the 2-thienyl derivative, the concurrent formation of tetra(3-thienyl)tin and tin (IV) iodide was also observed.

The Mössbauer spectra of the di(3-thienyl)tin dihalides (Table 2.2.4.) reveal the expected quadrupole-split doublets, and the magnitude of the quadrupole splitting is indicative of four co-ordinated tin, in unassociated, discrete, molecules. As for the related tri(3-thienyl)tin halides, the values of both the isomer shift and quadrupole splitting parameters are smaller than those of the related diphenyltin dihalides, but larger than those for di(2-thienyl)tin halides, implying intermediate electron-withdrawing properties for the 3-thienyl substituent. Both dichloride and dibromide have been characterised by the formation of 1:1 adducts with 2,2'-bipyridyl on treatment of the dihalide with an equimolar amount of 2,2'- bipyridyl in toluene solution. Mössbauer data for the complexes (Table 2.2.4) are consistent with a <u>cis</u> - octahedral structure for the dichloro complex but a distorted <u>trans</u> - octahedral geometry for the dibromo complex, by analogy with Mössbauer data for related complexes[50]. As expected, treatment of the di(3-thienyl)tin dichloride with p-tolylmagnesium bromide in ether gave di(3-thienyl) di(<u>p</u>-tolyl)tin (27), as a stable, recrystallisable solid.



(27)



(28)

The preparation and characterization of the related (3-furyl)tin systems, (28, n=2 or 3; X = Cl or Br), has also been achieved. The tri(3-furyl) tin chloride and bromide (28, n = 3) were obtained by the redistribution reactions of tetra(3-furyl)tin (3 mol) with the appropriate tin (IV) halide (1 mol) at 100-110° C for 1-2 hours. The resulting triorganotin halides 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 80K) show quadrupole-split doublets, without significant line broadening, having parameters (Table 2.2.5.) similar to those of the related (3-thienyl)- and phenyltin halides. Four co-ordination at tin is again inferred, and hence it would seem that these compounds are not associated to any significant extent in the solid state, despite the increased electronegativity of the heteroatom relative

TABLE 2.2.5.

$^{119}$Sn Mössbauer Data for (3-furyl)tin halides and Related compounds

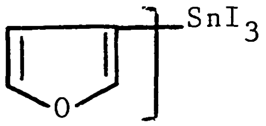
| Compound | Isomer Shift, (mm sec$^{-1}$ ± 0.02 | Quadrupole Splitting, (mm sec$^{-1}$ ± 0.02) |
|---|---|---|
| $(3\text{-}C_4H_3O)_3SnCl$ | 1.12 | 2.07 |
| $(3\text{-}C_4H_3O)_3SnBr$ | 1.18 | 2.03 |
| $(3\text{-}C_4H_3O)_3SnCl.Ph_3PO$ | 1.09 | 3.16 |
| $(3\text{-}C_4H_3O)_3SnBr.Ph_3PO$ | 1.12 | 3.12 |
| $(3\text{-}C_4H_3S)_3SnCl$ | 1.21 | 2.29 |
| $(3\text{-}C_4H_3S)_3SnBr$ | 1.25 | 2.08 |
| $(3\text{-}C_4H_3S)_3SnCl.Ph_3PO$ | 1.18 | 3.08 |
| $(3\text{-}C_4H_3S)_3SnBr.Ph_3PO$ | 1.21 | 3.03 |
| $(3\text{-}C_4H_3O)_2SnCl_2$ | 1.14 | 2.55 |
| $(3\text{-}C_4H_3O)_2SnBr_2$ | 1.23 | 2.19 |
| $(3\text{-}C_4H_3O)_2SnCl_2$.bipy | 0.76 | 2.02 |
| $(3\text{-}C_4H_3O)_2SnBr_2$.bipy | 0.83 | 2.13 |

a Relative to $BaSnO_3$

to the 3-thienyl analogues. Comparison of the Mössbauer data for these compounds with that for the related 3-thienyl- and phenyltin 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 electronegativity of the heteroatom. The isomer shift of tetra (2-furyl)tin is considerably lower than for tetra (3-furyl)tin, reflecting a reduced influence of the electronegative heteroatom at the 3-position. Thus it can be suggested that the 3-furyl substituent is less electron withdrawing than its 2-furyl analogue and that this in turn has a direct effect on the stability of derivatives of these compounds. It should be noted, however, that Mössbauer data cannot be used to forecast the potential stability of compounds when more than one variable has to be considered. Thus, for instance, the Mössbauer isomer shift for tetra(3-furyl)tin is smaller than that of tetra(2-thienyl)tin. If the isomer shift was solely a function of electron-withdrawing ability of the substituents at tin, (which in turn would relate to the stability of the compounds), the opposite result would be predicted.

Both the tri(3-furyl)tin bromide and chloride 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 again indicated by a significant reduction in the P=O infrared stretching frequency compared with that of the free ligand. The Mössbauer parameters of the adducts are very similar to those reported for the triphenylphosphine oxide complexes of triphenyl and tri(3-thienyl)tin halides discussed earlier, and similar structures can be assumed.

The related di(3-furyl)tin dihalides (28, $n = 2$) have also been obtained by appropriate redistribution reactions. As in the case of the other diheteroaryltin dihalides, these compounds are liquids. Four-co-ordinate, unassociated structures have been assumed from the Mössbauer parameters and isomer shifts reveal similar trends to those obtained for the tri-organotin halides in respect of the electron-withdrawing properties of the substituents at tin. Both the dichloride and the dibromide were characterised by the formation of 1:1 complexes with 2,2'-bipyridyl on treatment of the dihalide with an equimolar amount of the ligand in toluene solution. Mössbauer data for these complexes are consistent with <u>cis</u>-octahedral structures. The preparation of di(3-furyl)tin diiodide was also attempted by a redistribution reaction, and attempts were made to characterise this compound by complex formation with 2,2'-bipyridyl. However, analytical data and Mössbauer spectroscopy indicated that the product of redistribution was probably a mixture of the desired diiodide and (3-furyl)tin triiodide (29). This, together with the limited stability of the tri(3-furyl)tin bromide, may be some indication that the (3-furyl)tin halides do not enjoy the same degree of stability as their (3-thienyl) analogues.



(29)

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 coordination 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 thiopen to undergo rapid electrophilic substitution in the 2-position. The increased stability of the 3-heteroaryl derivatives is consistent with this point of view.

## 2.3 $^{119}$Sn N.m.r. solution studies of Heteroaryltin Compounds

Direct evidence of the instability of the (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 tri(2-furyl)tin chloride exhibited a signal at -164ppm, which on standing diminished in intensity while signals appeared at -260ppm and -110.9 ppm, arising from tetra(2-furyl)tin and di(2-furyl)tin dichloride, respectively. These signals increased in intensity with time. The corresponding tri(2-furyl)tin bromide is even less stable, no signal for this compound being observable. The spectrum of a freshly prepared solution of this compound (previously characterised in the "pure" state by Mössbauer spectroscopy) exhibited signals at -260 ppm and -205 ppm, attributable to tetra(2-furyl) tin and di(2-furyl)tin dibromide respectively.

These observations provide some insight into the difficulties encountered when trying to characterise the tri(2-heteroaryl)tin halides chemically. Both methods employed required the reactive substrate to be in solution prior to treatment with either a Grignard reagent, when attempting to prepare a mixed tetraorganostannane, or with a monodentate ligand, to form a stable complex.

The expected product of the redistribution reaction between tetra(2-furyl)tin (3 mol) and tin (IV) bromide (1 mol) is tri(2-furyl)tin bromide. In the absence of a solvent, a solid product crystallises, the Mössbauer parameters of which are consistent with those expected for the desired compound. However when this compound is dissolved in either toluene or chloroform and treated with a bidentate ligand e.g. 2,2' - bipyridyl, an insoluble complex is formed. The analytical data obtained for this complex indicate it to be the 2,2'-bipyridyl adduct of di(2-furyl)tin dibromide. Subsequent studies of the Mössbauer spectrum of this compound showed it to be identical to that of the authentic material. A similar pattern was observed in the solution behaviour of the tri(2-thienyl)tin halides, although the rate of disproportionation was much reduced compared with the 2-furyl analogues. As expected, the 3-heteroaryltin halides were found to be much more stable in solution, and did not appear to undergo disproportionation.

Thus the $^{119}$Sn n.m.r. experiment has provided some valuable information on the heteroaryltin compounds of interest in this study. A full range of $^{119}$Sn n.m.r. spectra have subsequently been obtained for both the 2- and 3-heteroaryltin halides previously discussed and also for a series of tetraheteroaryltin compounds, including the previously unknown tetra(benzo-b-thienyl)- and tetra(benzo-b-furyl)stannanes.

Some comparison of the $^{119}$Sn chemical shifts and Mössbauer data has also been made and will be discussed in terms of the possible elctronic properties of the heteroaryl groups. Additionally some solution studies of complex formation will be presented.

Prior to these results, however, it is important to consider some of the factors affecting the $^{119}$Sn chemical shift. Provided that there is no chemical interaction between the solvent and the solute, solvent and concentration effects usually do not exceed a few ppm, and therefore spectra obtained in non-coordinating solvents such as benzene, carbon tetrachloride and deuteriochloroform effectively relate to the pure substance. The lack of large changes in chemical shift with dilution in these solvents indicates that no complexation is occuring between sample and solvent, and that any possible self-association is absent, e.g., table 2.3.1.[56]. An increase in the coordination number at tin to five or six would increase the shielding of the tin nucleus and thereby produce a low frequency shift in the n.m.r. experiment. In the case of solvent effects and autoassociation, the origin of this shift is not yet fully understood. The additional ligand(s) should increase the diamagnetic term of neighbouring atoms, but this alone may not account for the large shifts observed. Additionally it is possible that complexation

Table 2.3.1

$^{119}Sn$ chemical shifts (ppm) for $Me_3SnCl$ dissolved in carbon tetrachloride[56]

| Concentration |  | Temperature (°C) |  |
|---|---|---|---|
| (mol%) | -5 | +20 | +35 |
| 40 | 159.5 | 159.5 | 159.6 |
| 20 | 160.7 | 160.6 | 159.9 |
| 10 | 159.9 | 159.7 | 159.8 |
| 5 | 159.8 | 159.6 | 159.2 |
| 3 | 159.8 | 159.5 | 159.7 |

reduces the effective nuclear charge at tin and hence reduces the paramagnetic contribution to the chemical shift or that some involvement of the tin 5d orbitals is taking place.

In discrete five and six coordinate tin complexes, an increase in the amount of s- character in the tin-carbon bonds is usually accompanied by a signal shift to low frequency.

The position of the $^{119}$Sn nmr signal is also heavily dependent on the nature of the substituents at tin. It is, generally assumed that the dominant factor contributing to the nuclear shielding is the paramagnetic term, $\sigma^P$ which can be expressed as:

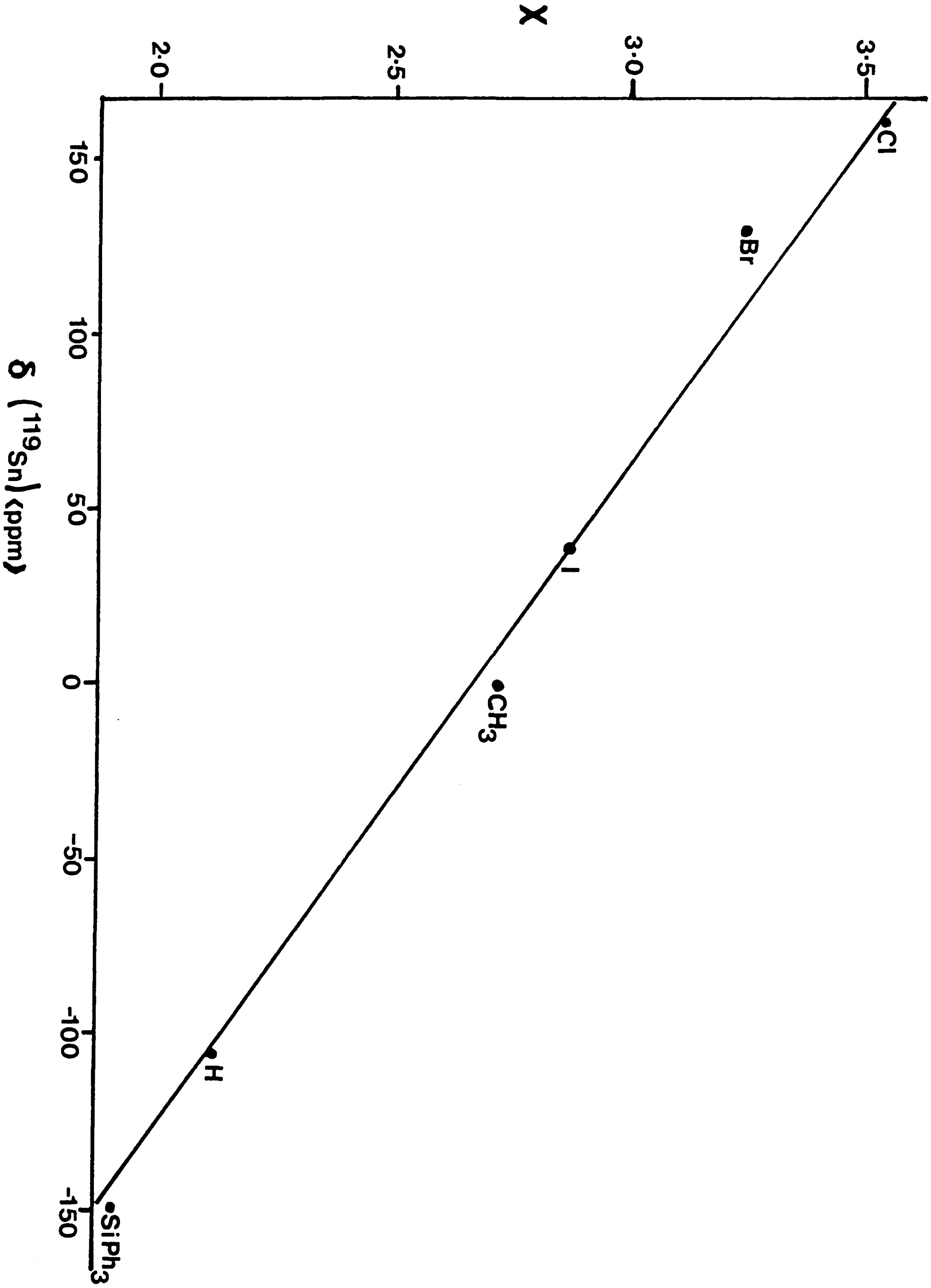
$$\sigma^P = \frac{-1}{\Delta E} [A < r^{-3} >_{5p} Q_{5p} + B < r^{-3} >_{5d} Q_{5d}]$$

where A and B are constants, $\Delta E$ is a mean electronic excitation energy and $< r^{-3} >$ is an average value of the appropriate radial function [57]. The values of Q depend on bond order and the imbalance of charge density in the appropriate orbitals, and are related to the effective nuclear charge of the tin atom. Withdrawal of electrons from tin will increase Q and, if other factors remain reasonably constant, then the tin shielding will decrease and hence $^{119}$Sn chemical shifts should become more positive, moving towards high frequency with increasing electronegativity of the groups attached to tin. For example, within a series of compounds, $R_nSnX_{4-n}$, the nature of both the organic group, R, and the anionic group, X, have a distinct bearing on the overall effect on the nucleus under investigation. In general, as the electron-releasing power of the R group increases, the shielding of the tin nucleus will also increase and result in a shift to lower frequencies. However, when a saturated R group is replaced by, e.g., phenyl, a shift to low frequency is also observed which is inconsistent with the greater electron-withdrawing power of phenyl. This effect has also been observed with benzyl, vinyl and allyl substituents and may be due to an increased polarisability of unsaturated substituents[56].

For a given series of compounds, $R_3SnX$, the $^{119}Sn$ chemical shift should move to higher frequency with increased inductive withdrawing power of X. For example, a plot of $\delta$ against Pauling electronegativity of X results in a good linear correlation (Fig. 2.3.1.[58]). Further examples of this effect are provided by series of related molecules where the point of variation is not adjacent to the tin atom; in the series $Me_3SnCH_nCl_{3-n}$, the $^{119}Sn$ shielding has been observed to decrease by 85 ppm as n changes from 3 to 0[59]. Additionally correlations have been noted between $^{119}Sn$ chemical shifts and the Hammett $\sigma$ constants for substituted aryl derivatives of tin[60].

Fig.2.3.1

Dependence of $^{119}$Sn chemical shifts ppm upon Pauling electronegativity $\chi$ of substituent for some $Me_3SnX$ compounds.



However, when the atom attached directly to tin is changed, other effects may predominate and it may be difficult to recognise the effect of substituent electronegativity, especially when more than one electron-withdrawing substituent is involved. It seems probable that in such instances the imbalance of p electrons has a significant role to play and that the contribution to the paramagnetic term will be greatest when two p orbitals of tin are filled and one is vacant or vice-versa. Thus the observed decrease in tin shielding when one or two substituents are more electron-withdrawing than the others is to be expected. It is thought to be for this reason that plots of $\delta$ ($^{119}$Sn) versus n in series of the type $R_{4-n}SnX_n$ often exhibit a characteristic U-shaped appearance, e.g.,Fig.2.3.2.[58]

It is well established that replacement of one group in $R_4Sn$, with an electron withdrawing group, X, will generally decrease the tin shielding. However, further replacement will reverse this trend and $\delta$ ($^{119}$Sn) in $SnX_4$ may well be more negative than for $R_4Sn$, despite the relative electronegativities of R and X. This behaviour is most extreme when X is bulky and polarisable, e.g.,I, but there is no consensus as to the origin of the effect[61].

Direct evidence of $p\pi$ - $d\pi$ overlap involving the 5d orbitals of tin as acceptors is hard to find, and any effect which this may have upon tin shielding is unclear.

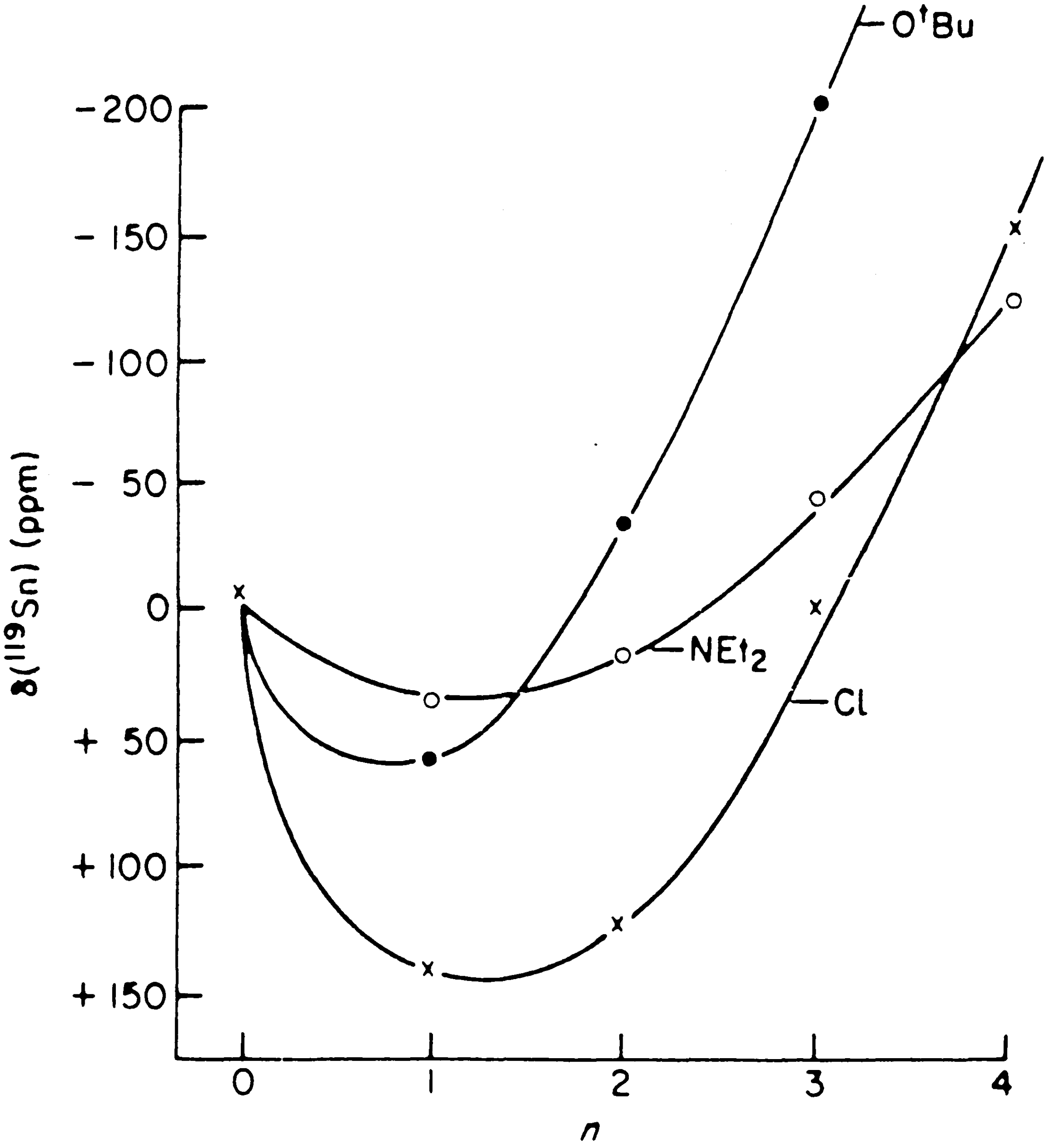


Fig. 2.3.2.

$^{119}$Sn Chemical shifts (ppm) for Unassociated Butyltin Compounds, $Bu_{4-n}SnX_n$ as a Function of n.

However, it is possible that such an occurrence would reduce the electronic imbalance in bonds to tin and thus reduce the paramagnetic term which in turn would lead to increased shielding[59,62,63]. The occurrence of pπ - dπ interactions has been suggested on a number of occasions where species with several electron-withdrawing substituents at tin have produced abnormally high shielding[64]. Similarly the shielding effect of unsaturated groups attached to tin also suggests that π - interactions involving the tin 5d orbitals and the π systems of groups such as phenyl may be important[65].

$^{119}Sn$ nmr chemical shifts for the heteroaryltin halides and their derivatives are given in tables 2.3.2. and 2.3.3. Related data for a series of tetraheteroarylstannanes are presented in table 2.3.4. In the course of this work a number of mono-organotin trihalides were observed, either as products of disproportionation of di(2-heteroaryl)tin dihalides, or as minor impurities present in the more stable systems. The $^{119}Sn$ nmr signals for these compounds (Tables 2.3.2. and 2.3.3.) exhibit considerable broadening due to quadrupolar interactions between the halogens and $^{119}Sn$ nmr signals, and occur at low frequency, consistent with the established apparent increase in shielding of the tin nucleus as the number of halogens increases. A plot of chemical shift data for a given series, $R_{4-n}SnX_n$, against the number of halogen

TABLE 2.3.2.

$^{119}$Sn Mössbauer and N.m.r. Data for 3-heteroaryltin halides and Related Compounds

| Compound | Isomer Shift, (mm sec$^{-1}$ ± 0.02) | Quadrupole Splitting, (mm sec$^{-1}$ ± 0.02) | Chemical Shift, (ppm rel to $Me_4Sn$) ± 0.5 ppm | N.m.r. Conditions |
|---|---|---|---|---|
| $(3\text{-}C_4H_3O)_3SnCl$ | 1.12 | 2.07 | -40.1 | $CDCl_3$; 5% |
| $(3\text{-}C_4H_3O)_3SnBr$ | 1.18 | 2.03 | -80.8 | $CDCl_3$; 20% |
| $(3\text{-}C_4H_3O)_3SnCl.Ph_3PO$ | 1.09 | 3.16 | -129.0 | $CDCl_3$; 5% |
| $(3\text{-}C_4H_3O)_3SnBr.Ph_3PO$ | 1.12 | 3.12 | -183.8 | $CD_2Cl_2$; 5% |
| $(3\text{-}C_4H_3S)_3SnCl$ | 1.21 | 2.29 | -70.3 | $CDCl_3$; 10% |
| $(3\text{-}C_4H_3S)_3SnBr$ | 1.25 | 2.08 | -100.6 | $CDCl_3$; 5% |
| $(3\text{-}C_4H_3S)_3SnCl.Ph_3PO$ | 1.18 | 3.08 | -147.6 | $CDCl_3$; 5% |
| $(3\text{-}C_4H_3S)_3SnBr.Ph_3PO$ | 1.21 | 3.03 | -167.0 | $CD_2Cl_2$; 5% |
|  |  |  | -209.2 | $CD_2Cl_2$; 5%; 0° |
| $Ph_3SnCl$ | 1.37 | 2.459 | -48.06 | $CD_2Cl_2$; |
| $Ph_3SnBr$ | 1.37 | 2.46 |  |  |

TABLE 2.3.2. Continued

| Compound | Isomer Shift, (mm sec$^{-1}$ ± 0.02) | Quadrupole Splitting, (mm sec$^{-1}$ ± 0.02) | Chemical Shift, (ppm rel. to $Me_4Sn$) ± 0.5 ppm | N.m.r. Conditions |
|---|---|---|---|---|
| $(3\text{-}C_4H_3O)_2SnCl_2$ | 1.14 | 2.55 | -8.8 | $CDCl_3$; 80% |
| $(3\text{-}C_4H_3O)_2SnBr_2$ | 1.23 | 2.19 | -102.7 | $CDCl_3$; 50% |
| $(3\text{-}C_4H_3O)_2SnCl_2$.bipy | 0.76 | 2.02 | - | Insoluble |
| $(3\text{-}C_4H_3O)_2SnBr_2$.bipy | 0.83 | 2.13 | - | Insoluble |
| $(3\text{-}C_4H_3S)_2SnCl_2$ | 1.23 | 2.55 | -38.6 | $CDCl_3$; 80% |
| $(3\text{-}C_4H_3S)_2SnBr_2$ | 1.30 | 2.30 | -113.7 | $CDCl_3$; 30% |
| $(3\text{-}C_4H_3S)_2SnCl_2$.bipy | 0.86 | 2.00 | - | Insoluble |
| $(3\text{-}C_4H_3S)_2SnBr_2$.bipy | 1.22 | 3.26 | - | Insoluble |
| $Ph_2SnCl_2$ | 1.34 | 2.89[c] | -32.0[b] | $CD_2Cl_2$ |
| $Ph_2SnBr_2$ | 1.43 | 2.54[d] |  |  |

TABLE 2.3.2. Continued

| Compound | Isomer Shift, (mm $sec^{-1}$ ± 0.02) | Quadrupole Splitting, (mm $sec^{-1}$ ± 0.02) | Chemical Shift, (ppm rel. to $Me_4Sn$) ± 0.5 ppm | N.m.r. Conditions |
|---|---|---|---|---|
| $(3\text{-}C_4H_3O)SnCl_3$ | - | - | -51.0 | $CDCl_3$;[e] |
| $(3\text{-}C_4H_3O)SnBr_3$ | - | - | -268.5 | $CDCl_3$;[e] |
| $(3\text{-}C_4H_3S)SnBr_3$ | - | - | -264.8 | $CDCl_3$;[e] |

Footnotes

Relative to $BaSnO_3$

Solvent; concentration w/v; ambient temperature except as otherwise stated.

a Ref. 41

b Ref. 59

c Ref 42

d Ref 43

e This compound was present as a redistribution product of the $R_2SnX_2$ species; see Text.

TABLE 2.3.3.

$^{119}$Sn Mössbauer and N.m.r. Data for 2-Heteroaryltin Halides and Related Compounds

| Compound | Isomer Shift, (mm sec$^{-1}$ ± 0.02) | Quadrupole Splitting, (mm sec$^{-1}$ ± 0.02) | Chemical Shift, (ppm rel. to $Me_4Sn$) ± 0.5 ppm | Conditions for N.m.r. study |
|---|---|---|---|---|
| $(2-C_4H_3O)_3SnCl$ | 1.14 | 2.14 | -164.0 | $CDCl_3$; 20% |
| $(2-C_4H_3O)_2SnCl_2$ | 1.10 | 2.09 | -110.9 | $CDCl_3$; 80% |
| $(2-C_4H_3O)_3SnBr$ | 1.17 | 2.19 | See Text | |
| $(2-C_4H_3O)_2SnBr_2$ | 1.17 | 1.80 | -205.0 | Neat Liquid |
| $(2-C_4H_3O)SnBr_3$ | - | - | -324.8[a] | $CDCl_3$; |
| $(2-C_4H_3S)_3SnCl$ | 1.13 | 1.99 | -64.4 | $CDCl_3$; 50% |
| $(2-C_4H_3S)_2SnCl_2$ | 1.14 | 2.06 | -39.3 | $CDCl_3$; 80% |
| $(2-C_4H_3S)SnCl_3$ | - | - | -77.6[a] | $CDCl_3$; |
| $(2-C_4H_3S)_3SnBr$ | 1.18 | 1.99 | -104.6 | $CDCl_3$; 5% |

TABLE 2.3.3. Continued

| Compound | Isomer Shift, (mm sec$^{-1}$ ± 0.02) | Quadrupole Splitting, (mm sec$^{-1}$ ± 0.02) | Chemical Shift, (ppm rel. to $Me_4Sn$) ± 0.5 ppm | Conditions for N.m.r. study |
|---|---|---|---|---|
| $(2\text{-}C_4H_3S)_2SnBr_2$ | 1.17 | 1.80 | -134.8 | $CDCl_3$; 5% |
| $(2\text{-}C_4H_3O)_2SnBr_2$.bipy | 0.98 | 2.85 | - | Insoluble |
| $(2\text{-}C_4H_3S)_2SnCl_2$.bipy | 0.75 | 1.69 | - | Insoluble |

Footnote

Relative to $BaSnO_3$

Solvent; concentration w/v; ambient temperature

a This compound was present as a redistribution product of the $R_2SnX_2$ species - see Text.

TABLE 2.3.4.

$^{119}$Sn Mössbauer and N.m.r. Data for Tetra(heteroaryl)tin Compounds

| Compound | Isomer Shift, (mm sec$^{-1}$ ± 0.02) | Chemical Shift, (ppm rel. to $Me_4Sn$) ± 0.5 ppm | N.m.r. Conditions |
|---|---|---|---|
| (a) $R_4Sn$ | | | |
| R = 2-furyl | 1.06 | -260.2 | $CDCl_3$; 10% |
| | | -266.3 | $C_5H_5N$; 10% |
| | | -276.1 | DMSO; 10% |
| R = 2-benzo b furyl | 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 = 2-benzo b thienyl | 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 | $CDCl_3$; 10% |

TABLE 2.3.4. Continued

| Compound | Isomer Shift, (mm sec$^{-1}$ ± 0.02) | Chemical Shift, (ppm rel. to $Me_4Sn$) ± 0.5 ppm | N.m.r. Conditions |
|---|---|---|---|
| (b) $R^1_nSnR^2_{4-n}$ | | | |
| $R^1$ = $R^2$ = 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% |

Footnote

Relative to $BaSnO_3$

= 0.00 mm sec$^{-1}$ for all compounds

Solvent; concentration w/v; at ambient temperature atoms reveals the familiar U-shaped curve previously noted for a range of other R groups, the position of the minimum depending on the nature of the halogen.

$^{119}$Sn nmr studies of the phosphine oxide adducts of the triheteroaryltin halides reveal the predicted increase in shielding of the tin nucleus upon complex formation with the electron donating ligand. Similar effects have been observed for the related complexes of triphenyltin halides[66]. The chemical shifts of these compounds are found to be concentration dependent, and also to some extent, temperature dependent. Fig. 2.3.3. shows the concentration dependence, at 33° C, for the tri(3-thienyl) tin chloride triphenylphosphine oxide complex in deuteriochloroform. This effect implies a mobile equilibrium in solution between uncomplexed four-coordinate triheteroaryltin halide and the pentacoordinate adduct, the observed upfield shift being consistent[56,61] with the increase in coordination number of the tin atom.

Although the difficulties inherent in the interpretation of trends in $^{119}$Sn nmr chemical shift data with changes in substituent are well recognised[56,57,61], 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 " $\pi$ - excessive" and assumed to be "electron-rich".

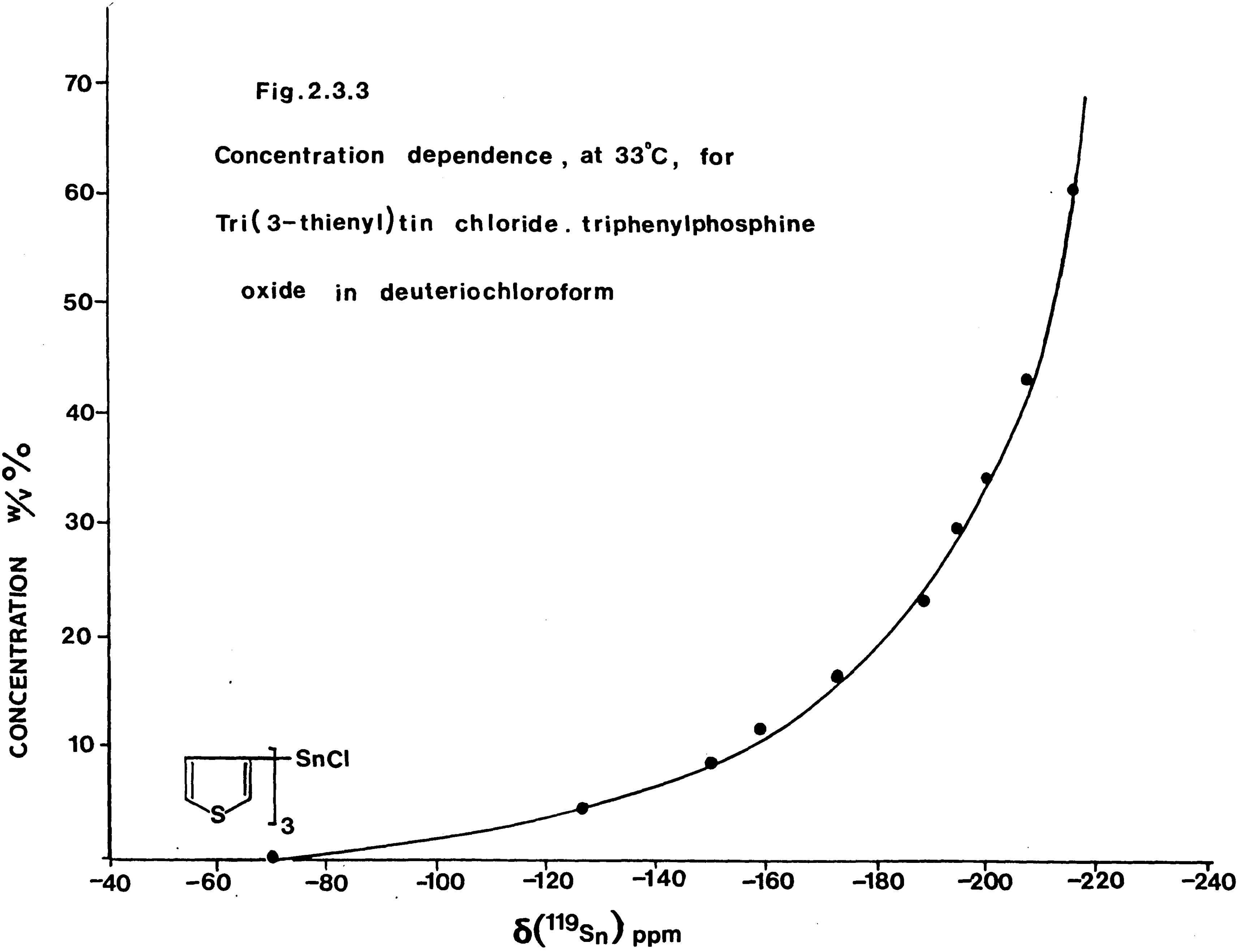


Fig.2.3.3

Concentration dependence, at 33°C, for Tri(3-thienyl)tin chloride. triphenylphosphine oxide in deuteriochloroform

However, this view is only valid where the $\pi$-system of the ring can interact in a conjugative manner with a substituent having a vacant orbital, with which $p\pi$ —— $p\pi$ or $p\pi$ —— $d\pi$ interactions can take place. It is possible that such substituents could therefore be involved in $p\pi$ —— $d\pi$ interactions with the tin atom, and this has been held responsible for the increased (diamagnetic) shielding of the tin atom in the series $Me_{4-n}Sn(2\text{-furyl})_n$ as the number of 2-furyl substituents is increased[67]. In this present study a parallel trend occurs in the series $(p\text{-tolyl})_{4-n}Sn(3\text{-thienyl})_n$ as the p-tolyl groups are replaced by the more "$\pi$-excessive" 3-thienyl system (Table 2.3.4). Similar increases in the shielding of the tin nucleus are observed in the series $Et_{4-n}SnZ_n$ (n=0-4, Z = phenyl, vinyl or $-C \equiv H$) where the alkyl groups are replaced by the $\pi$ systems, again suggesting that $\pi$-interactions with the tin 5d orbitals may be of some importance[65]. It has been pointed out, however, that it is far from clear as to the effect which such $\pi$-bonding might have upon the tin-shielding, although it is likely that it would reduce the paramagnetic term[61], usually considered to be the dominant factor contributing to the nuclear shielding[57].

The above heteroaryl substituents, due to the presence of the electronegative heteroatom, are also able to function as $\sigma$ electron-withdrawing systems, and many instances of this have been noted in the chemistry of Group V elements, notably phosphorus and arsenic[47]. Such electronegativity effects of directly-bonded substituents are known to be complex[56,61]. Not only would such substituents encourage synergic $p\pi \longrightarrow \mathrm{Sn}d\pi$ back donation, but intermolecular $\sigma$- coordination involving the tin atom would also be possible. However, the latter would be expected to result in concentration dependent $^{119}$Sn nmr data, and this has not been observed in the present study. Any interpretation of the effects of such heteroaryl substituents is therefore fraught with difficulty.

It is accepted that the $^{119}$Sn Mössbauer shifts reflect the 5s electron density at the Sn nucleus, and that a decrease in the isomer shift indicates electron withdrawal from tin. However, occupation of tin 5d orbitals as a result of $\pi$ - bonding may also cause a decrease in 5s electron density at the nucleus as a result of increased atomic core shielding.

A comparison of Mössbauer and $^{119}$Sn nmr parameters for a range of tetraheteroaryltin compounds is presented in table 2.3.4. In general it is of interest to note that substituents which result in a lowering of the $^{119}$Sn Mössbauer isomer shift (implying electron withdrawal and/or $\pi$ - bonding to tin) have the effect of increasing the shielding of the tin atom in the nmr experiment and moving the resonance to lower frequency. Thus, for example tetra(2-furyl)tin has a significantly reduced Mössbauer isomer shift compared to tetraphenyltin (and the lowest value of $\delta$ in the series), and yet has the most shielded tin nucleus in the nmr experiments. The slightly higher degree of nuclear shielding in tetra(3-thienyl)tin compared with tetra(3-furyl)tin may point to some degree of synergic $\pi$ - bonding in these compounds. A similar inverse correlation between Mössbauer isomer shifts and $^{119}$Sn nmr chemical shifts is also apparent (but to a lesser degree) in the heteroaryltin halides.

Additional evidence of the electron-withdrawing properties of the above heteroaryl substituents in the tetraheteroarylstannanes has been sought. Tetraorganostannanes show very weak acceptor properties and do not form solid adducts with donor molecules, with the possible exception of trifluoromethyltrimethylstannane which is reported[68] to form a 1:1 complex with hexamethylphosphorustriamide. In addition it is interesting to note that the $^{119}$Sn nmr chemical shift of tetrakis (*m*-trifluoromethylphenyl)stannane in DMSO shows a 10ppm shift to low frequency (increased shielding) compared to that in deuteriochloroform[69] whereas a low frequency shift of only 1.6ppm is found for tetramethyltin in similar solvents[70]. For tetra(2-furyl)tin, a low frequency shift of 16ppm is found when deuteriochloroform is replaced by DMSO. Similarly when pyridine is used ~~as the solvent, there is a 6ppm shift to low frequency,~~ (see table 2.3.4. ). Using the same solvent systems, comparable upfield shifts have been observed for tetra(2-thienyl)tin and, to a lesser extent, for tetra(3-furyl)tin. However, it was noted that these shifts appeared 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 $\sigma$ electron-withdrawing properties of the 2-thienyl and 2-furyl substituents. In contrast, addition of triphenylphosphine oxide to a deuteriochloroform solution of tetra(2-furyl)tin causes no shift in the $^{119}$Sn nmr signal. However, when tetra(2-furyl)tin and triphenylphosphine oxide are melted together, the Mössbauer 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 that $p\pi$ —— $d\pi$ effects may, in addition, have a role to play in the interaction between such ring systems and tin.

Using the pairwise additivity model[71,72], it is possible to predict the $^{119}$Sn nmr chemical shifts of a series of mixed tetraorganostannanes ($R^1_nR^2_{4-n}Sn$) from the data for $R^1_4Sn$ and $R^2_4Sn$. In general the substituent effect in the nmr experiment has been found to be pairwise additive, the pairwise contributions arising because each group suffers a linear correction due to the presence of each neighbouring substituent. The model recognises the changes caused by the substituent on the wave functions of neighbouring substituents and allows calculation of the chemical shift by summing the pairwise interactions of all the substituents taken as adjacent pairs. In tetrahedral compounds the chemical shift of the central atom is calculated by summing pairwise interactions along the six edges of the tetrahedron. For example, in $R_4Sn$ the pairwise interaction between two R groups is equivalent to 1/6 of the chemical shift for the parent compound. Similarly from the chemical shift of $R^1{}_4Sn$ a value for the $R^1 - R^1$ interaction can be achieved. An approximation of the $R^1 - R^1$ interaction can now be obtained by averaging the two. However, should the chemical shift data be available for an additional member of the $R_nSnR^1{}_{4-n}$ series, an improved figure for the $R^1 - R^2$ effect may be derived.

For tetra(3-thienyl)tin the observed chemical shift was found to be - 168.7ppm, and thus the (3-thienyl) - (3-thienyl) interaction can be calculated as -28.1ppm. Similarly a value of -20.55ppm can be obtained for a (p-tolyl) - (p-tolyl) effect. An average of these two parameters can be said to approximate to amixed (p-tolyl) - (3-thienyl) interaction, and thus estimates of the $^{119}Sn$

nmr chemical shifts for the series (3-thienyl)$_n$Sn(*p*-tolyl)$_{4-n}$ can be obtained. The prediction of chemical shifts by this model is supported by the experimental data obtained for di(3-thienyl)di(*p*-tolyl)tin and tri(3-thienyl)-*p*-tolyltin, experimental figures of -146.3 and -157.8ppm respectively comparing well with calculated values of 146.0 and -157.4ppm. Further it is possible to use this, most recent, experimental data to gain the best possible estimate for the (3-thienyl) -(*p*-tolyl) interaction parameter:

Tri(3-thienyl)*p*-tolyltin $\equiv$
[3 x (thienyl-thienyl) interactions]
+ [3 x (thienyl-tolyl) interactions]

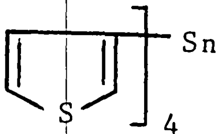
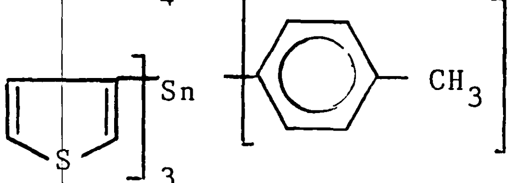
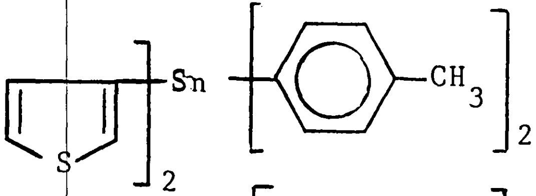
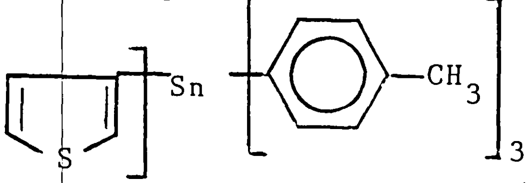
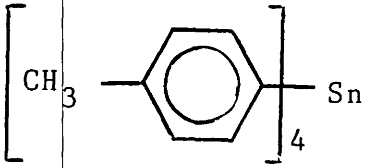
$$\text{Hence } \frac{-157.8 - (3 \times -28.1)}{3} \equiv \text{(thienyl-}p\text{-tolyl)} = -24.5\text{ppm}$$

Also
Di(3-thienyl)di(*p*-tolyl)tin $\equiv$
[1 x (thienyl-thienyl) interaction]
+ [1 x (*p*-tolyl-*p*-tolyl) interaction]
+ [4 x (*p*-tolyl-thienyl) interactions]

$$\text{Hence } \frac{-146.3 + 28.1 + 20.55}{4} \equiv \text{(thienyl-}p\text{-tolyl)} = -24.41\text{ppm}$$

The average of the two values for the (*p*-tolyl)-(3-thienyl) interaction approximates to -24.46ppm, and the best estimate for the chemical shift of tri(*p*-tolyl)3-thienyltin becomes -135.0ppm. Table 2.3.5. allows a comparison of experimental and calculated data, including the revised calculation of the predicted chemical shift of tri(_p_-tolyl)3-thienyltin.

TABLE 2.3.5.

| | Expt. | Calc$^a$ | Calc$^b$ |
|---|---|---|---|
|  | -168.7 | | |
|  | -157.8 | -157.4 | -157.7 |
|  | -146.3 | -146.0 | -146.5 |
|  | | -134.6 | -135.0 |
|  | -123.3 | | |

## 2.4. Experimental

### Mössbauer Data

$^{119}$Sn Mössbauer spectra were obtained using a constant acceleration spectrometer. A 15m Ci $BaSnO_3$ source was used at room temperature, the samples sealed in perspex discs and cooled to 80K using a continuous flow nitrogen cryostat with helium exchange gas. The Mössbauer 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 Fig. 2.4.1. The theoretical aspects of Mössbauer spectroscopy are discussed in an appendix to this Thesis.

### $^{119}$Sn NMR Measurements

$^{119}$Sn nmr 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[73]. Field frequency lock was to external $D_2O$. Chemical shifts are relative to $Me_4Sn$ and are accurate to ± 0.5 ppm.

### $^1$H NMR Measurements

$^1$H NMR spectra were recorded at 80MHz using a Brüker WP80 SY FT spectrometer, using TMS as internal standard.

## Mass Spectra

Mass Spectra were recorded at 70eV with an AEI MS30 spectrometer.

## Infrared Measurements

Infrared spectra were recorded either as potassium bromide discs or nujol mulls using a Pye Unicam SP.200 instrument.

All the reactions described were carried out under an inert atmosphere of either nitrogen or argon. All solvents employed were redistilled and dry.

## Preparation of Tetraorganotin Compounds

### Tetra-(2-thienyl)tin

Butyllithium (1.6 mol dm$^{-3}$ in hexane, 77.7 cm$^3$, 0.123 moles) was added, dropwise, to thiophen (15g, 0.179 moles) in ether (100 cm$^3$), with cooling (ice), and stirred for 1 hr. Tin (IV) chloride (6.46g, 2.48 x 10$^{-2}$moles), in hexane, was slowly added to the reaction mixture. On completion of the addition, the reaction mixture was maintained under reflux for 1 hr. After cooling, the reaction mixture was hydrolysed with saturated aqueous ammonium chloride, the crude solid product filtered and washed with water. The crude product was recrystallised from ethanol to yield 3.63g, (36%) of white needle-like crystals, m.p. 158-159$^{\circ}$ (Lit.,[74] 156$^{\circ}$).

### Tetra (2-furyl)tin

Butyllithium (1.6 mol. dm$^{-3}$, in hexane, 80cm$^3$, 0.128 moles) was added, dropwise to furan (10g, 0.147 moles) in dry ether (100cm$^3$), with cooling (ice/salt) and the resulting solution stirred for 1 hr. Tin(IV)chloride (6.5g, 2.49 x 10$^{-2}$ moles), in hexane, was slowly added to the reaction mixture with continued stirring. On completion of the addition, the reaction mixture was allowed to warm to room temperature and then heated to reflux for 1 hr. After cooling, the reaction mixture was hydrolysed, filtered, separated and the organic layer evaporated to yield an orange crystalline solid. Recrystallisation from hexane provided a white crystalline solid, 3·21g, (33%), m.p. 75-77° (Lit.,[52] 68-69°)

## Tetra-(3-thienyl)tin

Butyllithium (1.38 mol $dm^{-3}$, in hexane, 111$cm^3$ 1.53 x $10^{-1}$ moles) was cooled to -70° C ($CO_2$/acetone). Dropwise addition of 3-bromothiophen (25g, 1.53 x $10^{-1}$ moles), in ether, was carried out over a period of 1 hr. Tin (IV)chloride (4.5$cm^3$, 10.02g, 3.84 x $10^{-2}$ moles, in hexane, was added dropwise at -70° C. On completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred for 3 hrs. The resultant white suspension was poured into water and stirred, the solid washed and recrystallised from ethanol to yield a crop of fine, white, needle-like crystals, 8.3g, (48%) m.p. 224-227°(Lit.,[52]220-222°, from DMSO).

## Tetra-(3-furyl)tin

Butyllithium (1.48 mol $dm^{-3}$, in hexane, 45 $cm^3$, 6·66 x $10^{-2}$ moles) was slowly added to 3-bromofuran (9·8g,

$6.67 \times 10^{-2}$ moles) in ether (50 $cm^3$ at -70° C. Tin(IV)chloride (4.30g, 1.9 $cm^3$, $1.65 \times 10^{-2}$ moles), in hexane (20 $cm^3$) was added dropwise and the reaction mixture stirred at -70° C for 3 hrs. The reaction mixture was allowed to warm to room temperature, evaporated to dryness and extracted with toluene. Evaporation of the toluene solution produced a solid residue which on recrystallisation from hexane yielded a crop of fine, white, needle-like crystals, 2.72 (42%), m.p. 90-92° (lit.,[52] 102-104°).

Tetra (2-benzo-[b]-thienyl)tin

Butyllithium (1.48 mol $dm^{-3}$, 75 $cm^3$, $1.11 \times 10^{-1}$ moles) was added dropwise to benzo- b -thiophen (17g, $1.27 \times 10^{-1}$ moles) in dry ether (50 $cm^3$) with ice cooling. The reaction mixture was stirred at room temperature for 2 hrs. Tin (IV)chloride (3.0 $cm^3$, $2.60 \times 10^{-2}$ moles in hexane) was added dropwise with continued stirring, the reaction mixture heated under reflux for a further 2 hrs. and hydrolysed by pouring into water with vigorous stirring. The solid product was filtered, alkali-washed and recrystallised from toluene, m.pt. 254-257° C. Yield 9.90g (59%). Found : C, 59.60: H, 3.15; S, 18.95; $C_{32}H_{20}S_4Sn$ requires C, 59.00; H, 3.10; S, 19.70%.

Tetra(2-benzo-[b]-furyl)tin

Butyllithium (1.48 mol dm$^{-3}$, 60 cm$^{3}$, 8.88 x 10$^{-2}$ moles) was added dropwise to benzo-b -furan (12g, 1.02 x 10$^{-1}$ moles) in ether (50 cm$^{3}$) with cooling (ice/salt) and stirred for 3 hrs. Tin (IV)chloride (2.4 cm$^{3}$, 2.08 x 10$^{-2}$ moles) was added dropwise as a hexane solution and the reaction mixture stirred under reflux for a further 2 hrs. After cooling, the product was hydrolysed, filtered, alkali washed and recrystallised from toluene, m.pt. 231.5 - 233$^{o}$ C. Yield 7.85g (64%). Found : C, 65.85; H, 3.55; $C_{32}H_{20}O_{4}Sn$ requires C, 65.45; H, 3.45%.

Tetra(p-tolyl)tin

Butyllithium (1.5 mol dm$^{-3}$, in hexane, 39 cm$^{3}$, 5.85 x 10$^{-2}$ moles) was added dropwise, with stirring, to an ether solution of *p*- bromotoluene (10g, 5.85 x 10$^{-2}$ moles), with cooling ($CO_2$/acetone). Stirring was continued and tin(IV)chloride (1.7cm$^{3}$, 3.78g, 1.45 x 10$^{-2}$ moles was added dropwise as a hexane solution. The reaction mixture was maintained at -70$^{o}$ C for 1 hr and then allowed to warm to room temperature. On hydrolysis, a solid persisted, which when recrystallised from a toluene/ethanol mixture, yielded a white crystalline material, 3.1g, (44%) m.p. 238$^{o}$, (lit.,[75,76] 238$^{o}$).

## Preparation of Model Phenyltin Compounds

### Triphenyltin Chloride (by Redistribution)

Tetraphenyltin (3g, 7.03 x $10^{-3}$ moles) and tin(IV) chloride (0.6g, 2.31 x $10^{-3}$ moles) were heated together at 200° C for 1½ hrs, with stirring. On cooling, the melt crystallised and recrystallisation from iso-propyl alcohol provided white crystals, 0.3g (39%), m.p. 104.5-106° (lit.,[78] 105.5-107°).

### Diphenyltin Dichloride (by Redistribution)

Tetraphenyltin (1g, 2.34 x $10^{-3}$ moles) and tin(IV) chloride (0.6g, 2.31 x $10^{-3}$ moles) were heated together for 1 hr at 150-160° C. On cooling, a low melting solid crystallised, m.p. 42°, (lit.,[77] 42-44°).

### Triphenyltin Chloride (*via* the use of mercury (II) chloride)

Mercury (II) chloride (0.543g, 2.0 x $10^{-3}$ moles), in methanol, and tetraphenyltin (0.853g, 2.0 x $10^{-3}$ moles), in THF, were stirred together in the cold, in the absence of light for 3 hrs. On hydrolysis of the reaction mixture with aqueous sodium chloride (10cm$^3$, 0.1 mol dm$^{-3}$) a white solid persisted, (phenylmercury chloride m.p. 235° (crude), lit.,[78] 258°). Subsequently, the filtrate was extracted into chloroform. After drying, evaporation of the chloroform layer yielded triphenyltin chloride which was then recrystallised from isopropanol, m.p. 102-105°, (lit.,[77] 105.5-107°).

## Triphenyltin Bromide

Tetraphenyltin (0.5g, $1.17 \times 10^{-3}$ moles) and tin(IV)bromide (0.17g, $3.88 \times 10^{-4}$ moles) were melted together in the absence of any solvent at 220° C for 1hr. On cooling, a crystalline solid was formed. This was subsequently extracted into chloroform to remove any unreacted tetraphenyltin, the chloroform extract evaporated and the residue recrystallised from isopropanol to yield fine white crystals, m.p. 118.5-121° (lit.,[79] 118-120°).

## Triphenyl(p-tolyl)tin

Triphenyltin chloride (2.0g, $5.19 \times 10^{-3}$ moles), previously prepared by the redistribution reaction, was treated with a Grignard reagent, prepared from *p*-bromotoluene (1.78g, $1.04 \times 10^{-2}$ moles) and magnesium (0.35g, $1.44 \times 10^{-2}$ moles) in tetrahydrofuran (10cm$^3$). The reaction mixture was hydrolysed using saturated aqueous ammonium chloride, filtered and the non-aqueous layer separated, dried over anhydrous magnesium sulphate and evaporated. The residue was recrystallised from isopropanol. Yield 1.2g (54%), 121-122° (lit.,[80] 124°).

## Exploration of Routes to Heteroaryltin Halides

### Attempted Preparation of Tri-(2-thienyl)tin Chloride using Mercury (II) Chloride

Tetra-(2-thienyl)tin (0.5g, $1.11 \times 10^{-3}$ moles) and mercury (II) chloride ( 0.301g, $1.11 \times 10^{-3}$ moles) were stirred together overnight in the cold, in the absence of light, in various solvents. When methanol was used as the solvent for the mercury (II) salt and tetrahydrofuran for the stannane, the residue obtained on evaporation was extracted with isopropanol. The soluble fraction was once more evaporated and the solid obtained recrystallised from acetone to yield 2-thienylmercury (II) chloride as a white crystalline materials, m.p. 183° (lit.,[81] 183°). However, the remaining insoluble substance was found, by Mössbauer spectroscopy, to contain tin only in the form of tin(IV)oxide. Thus, it would appear that the protic solvent, methanol, may have facilitated the cleavage of tin-carbon bonds in the required compound. However, when the dipolar aprotic solvent, dimethylformamide, was employed as the sole solvent for the same reaction, a different mercury (II) compound was formed. As previously, the reaction mixture was stirred overnight in the cold and in the absence of light. During this time, di-(2-thienyl) mercury precipitated from the solution as a white crystalline solid m.p. $197^{\circ}$, (lit.,[82] $198-199^{\circ}$). A mass spectrum was obtained on the residue from evaporation of the dimethyl formamide-soluble fraction, but was of little assistance due to the complexity of the mixture, signals from both tin and mercury species being apparent. When the reaction was carried out in tetrahydrofuran, an insoluble, high melting material was isolated during work-up. This was subsequently found to contain tin only in the form of tin(IV)oxide, by Mössbauer spectroscopy. Mass spectra provided evidence for mercury being present in the supernatant liquid as both di-(2-thienyl)mercury and (2-thienyl)mercury chloride.

## Reactions of Tetra-(2-furyl)tin with Mercury(II)Chloride

Tetra-(2-furyl)tin (0.5g, $1.29 \times 10^{-3}$ moles) was treated with mercury(II)chloride (0.351g, $1.29 \times 10^{-3}$ moles) under the same conditions as for the 2-thienyl analogue. From the methanol/tetrahydrofuran system, an insoluble amorphous powder was isolated and subsequently identified as tin(IV)oxide by the Mössbauer technique. The mercury compound was identified as (2-furyl) mercury chloride following extraction and recrystallisation from ethanol m.p. 151-152°, (lit.,[83] 151°), m/e 304 ($M^+$, 202 Hg, $^{35}Cl$). Using tetrahydrofuran as the sole reaction solvent, evaporation of the reaction mixture produced an orange oil. The mass spectrum of this crude material suggested a mixture of at least four species: tri-(2-furyl)tin chloride, di-(2-furyl)tin dichloride, (2-furyl)mercury chloride and di-(2-furyl)mercury. However, in subsequent work, only the (2-furyl) mercury chloride could be isolated in the pure state, m.p. 149°, (lit.,[83] 151°). On addition of hexane to the above oil, the insoluble tin (IV) oxide was precipitated. When the reaction was conducted in dimethyl formamide, the solvent was evaporated to leave an orange oil. The mass spectrum of the oil was indicative of the formation of di-(2-furyl) mercury and a mixture of (2-furyl)tin (IV) chlorides. Only the di(2-furyl)mercury compound could be isolated from the mixture by recrystallisation from ethanol, m.p. 110-112°, (lit.,[83] 114°).

## Reactions with Halogens

### Tetra(2-thienyl)tin with Iodine

Tetra(2-thienyl)tin(10.5g, $1.11 \times 10^{-3}$ moles) was treated with iodine (0.28g, $1.10 \times 10^{-3}$ moles) in chloroform (5 $cm^3$), overnight, with stirring, in the cold. The iodine colouration disappeared. The solution was evaporated, leaving a greyish crystalline solid, having a melting point of approximately 50° C. More accurate melting point data could not be obtained due to the instability of this compound to the atmosphere.

### Reactions between Tetra-(2-furyl)tin and Iodine and Bromine

Tetra(2-furyl)tin (0.5g, $1.29 \times 10^{-3}$ moles) was treated with iodine (0.33g, $1.30 \times 10^{-3}$ moles). Similarly, the same quantity of tetra(2-furyl)tin was reacted with bromine (0.21g, $1.31 \times 10^{-3}$ moles). In both cases chloroform was used as the solvent and the reaction mixtures stirred overnight in the cold. In the iodine reaction, an investigatory thin layer chromatogram revealed the presence of unreacted tetra(2-furyl)tin, together with monoorganic and/or inorganic tin species. The tin species were visualised with catechol violet (catechol sulphonphthalein). The same species were apparent in the reaction of bromine, despite a controlled addition of the bromine to tetra-(2-furyl)tin.

### Reaction of Tetra-(2-thienyl)tin with Iodine Monochloride

A chloroform solution of iodine monochloride (0·18g, $1{\cdot}11 \times 10^{-3}$ moles) was added dropwise to a chloroform solution of tetra(2-thienyl)tin (0.5, 1.11 x $10^{-3}$ moles) with stirring and ice/salt cooling. The initial pink colouration quickly faded. Following partial evaporation, a white solid gradually precipitated. Extraction of this solid with dry hexane produced two or three brick-like transparent crystals. Mass spectral evidence was supportive of the presence of the required triorganotin halide, m/e 404 ($M^+$ $^{120}Sn$, $^{35}Cl$). Despite varying the conditions of the reaction, formation of the crystals could not be reproduced. Additionally, they were found to be unstable to the atmosphere and further analytical studies were precluded. The final decomposition product was found to be tin(IV)oxide by Mössbauer spectroscopy. The major product of the reaction was not positively identified but was observed to be less polar than the tetraorganotin starting material by thin layer chromatography.

## Preparation of Triheteroaryltin Halides

Tri-(3-thienyl)tin chloride  Tetra-(3-thienyl)tin (1.0 g, $2.2 \times 10^{-3}$ moles) and tin(IV)chloride ($0.08\ cm^3$, $7.81 \times 10^{-4}$ moles) were heated together with stirring at an oil bath temperature of 120° for 1 hr. The product crystallised on cooling, and was recrystallised from hexane-toluene, m.p. 103-104.5°. Anal. Found: C, 35.75; H, 2.15; S, 23.95. $C_{12}H_9ClS_3Sn$ requires: C, 35.70; H, 2.25; S, 23.85%.

Tri-(3-thienyl)tin bromide  Tetra-(3-thienyl)tin (0.75 g, $1.66 \times 10^{-3}$ moles) and tin(IV)bromide (0.24 g, $5.48 \times 10^{-4}$ moles) were heated together with stirring at an oil bath temperature of 170° for 1 hr. On cooling, the crude product was recrystallised from hexane-toluene, m.p. 115°. Anal. Found: C, 32.30; H, 2.15; S, 21.15. $C_{12}H_9BrS_3Sn$ requires: C, 32.15; H, 2.05; S, 21.45%.

Tri-(3-thienyl)tin iodide  Tetra-(3-thienyl)tin (1.0 g, $2.2 \times 10^{-3}$ moles) and tin(IV)iodide (0.46 g, $7.34 \times 10^{-4}$ moles) were heated together in toluene ($7.5\ cm^3$) under reflux for 3 days. The colour of the solution gradually changed from orange to yellow. TLC indicated that some unreacted tetra-3-thienyltin was still present.

On cooling, crystals were deposited, which were filtered and extracted with hot chloroform. Evaporation of the chloroform extracts gave a solid which was recrystallised from hexane-toluene, m.p. 127-8°. Anal. Found: C, 29.35; H, 1.80; S, 19.90; I, 25.75. $C_{12}H_9IS_3Sn$ requires: C, 29.10; H, 1.85; S, 19.45; I, 25.65%.

Tri(3-furyl)tin bromide

Tetra(3-furyl)tin (0.5g, $1.29 \times 10^{-3}$ moles) and tin(IV) bromide (0.19g, $4.33 \times 10^{-4}$ moles) were heated together, with stirring, at an oil bath temperature of 110° C for 1 hr. The product crystallised on cooling and was recrystallised from hexane to yield 0.28g of white crystals which showed gradual signs of decomposition (darkening) on standing for several days, m.pt. 77.5-80° C. Found: C, 35.70; H, 2.15; Br, 20.65; $C_{12}H_9BrO_3Sn$ requires C, 36.05; H, 2.25; Br, 20.00%.

Tri(3-furyl)tin chloride

Tetra(3-furyl)tin (1.0g, $2.58 \times 10^{-3}$ moles) and tin(IV) chloride (0.1 ml, $8.68 \times 10^{-4}$ moles) were heated together with stirring at an oil bath temperature of 100° C for 2 hrs. The product crystallised on cooling and was purified by recrystallisation from hexane to give 0.45g of white crystals, m.pt. 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, 10.00%.

## Preparation of Tri(2-Thienyl)- and Tri-(2-Furyl)tin halides

These were prepared by redistribution reactions between the tetra-(2-heteroaryl)stannane and the appropriate tin(IV)halide, under conditions similar to those used as described above for the preparation of the tri-(3-furyl)- and tri-(3-thienyl)tin halides. Immediately following their preparation, the compounds were sealed in perspex discs, and the Mössbauer spectra recorded at 80 K. Attempts to purify these compounds by recrystallisation were unsuccessful.

## Chemical Characterisation of Triheteroaryltin Halides

### Triphenylphosphine oxide complexes of tri-(3-thienyl)tin Halides

A solution of the tri(3-thienyl)tin halide in toluene was treated in the cold with stirring with an equimolar amount of triphenylphosphine oxide, also dissolved in toluene. The following complexes crystallised from the solutions:

(a) Tri-(3-thienyl)tin chloride. $Ph_3PO$, m.p. 142-4°. Anal. Found: C, 53.00; H, 3.60; Cl, 5.00; $C_{30}H_{24}ClOPS_3Sn$ requires: C, 52.85; H, 3.55; Cl, 5.20%.
Infrared (Nujol mull) : 1145 $cm^{-1}$ and 1122 $cm^{-1}$ (co-ordinated P=O)

(b) Tri-(3-thienyl)tin bromide. $Ph_3PO$, m.p. 137-40°. Anal. Found: C, 49.65; H, 3.35; S, 13.40. $C_{30}H_{24}BrOPS_3Sn$ requires: C, 49.60; H, 3.35; S, 13.25%.
i.r. (nujol mull) : 1140 and 1119 $cm^{-1}$ (co-ordinated P=O)

(c) Tri-(3-thienyl)tin iodide. $Ph_3PO$, m.p. 138-9°. Anal. Found: C, 46.59; H, 3.11; S, 12.21; $C_{30}H_{24}IOPS_3Sn$ requires: C, 46.00; H, 3.13; S, 12.44%.

Tri-(3-thienyl)(p-tolyl)stannane Tri-(3-thienyl)tin chloride (0.68 g, 1.69 x $10^{-3}$ moles) was dissolved in dry THF (5 $cm^3$) and treated with a solution of the Grignard reagent prepared from *p*-bromotoluene (0.56 g, 3.39 x $10^{-3}$ moles) and magnesium (0.1 g, 4.11 x $10^{-3}$ moles) in THF (8 $cm^3$). The resulting reaction mixture was stirred overnight, and then hydrolysed with aqueous ammonium chloride. The organic layer was separated, dried, and evaporated. The residue was recrystallised from isopropanol to give crystals, m.p. 119-21°. Anal. Found: C, 49.50; H, 3.45; S, 20.95; $C_{19}H_{16}S_3Sn$ requires: C, 49.7; H, 3.50; S, 20.95. $^1H$ n.m.r. ($CDCl_3$)$\delta$: 7.1-7.9, (m, 13 ArH); 2.35 (s, 3H) ppm.

### Triphenylphosphine oxide complexes of tri(3-furyl)tin halides

A toluene solution of the tri(3-furyl)tin halide was treated in the cold, with stirring, with an equimolar amount of triphenylphosphine oxide, also dissolved in toluene. The following complexes crystallised out on ice-cooling with the dropwise addition of hexane:

(a) Tri(3-furyl)tin chloride - $Ph_3PO$ m.pt. 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%. Yield : 73%. Infrared (nujol mull) : 1158 $cm^{-1}$ (co-ordinated P=O).

(b) Tri(3-furyl)tin bromide - $Ph_3PO$ m.pt. 134-135° C
Found : C, 53.10; H, 3.50; Br, 11.85; P, 4.75; $C_{30}H_{24}BrO_4PSn$ requires C, 53.15; H, 3.55; Br, 11.80; P, 4.55%. Yield : 80%
Infrared (nujol mull) : 1145 $cm^{-1}$ (co-ordinated P=O).

## Triphenylphosphine oxide complexes of tri(2-thienyl)-tin halides

### a) Tri(2-thienyl)tin chloride $Ph_3PO$

Tetra(2-thienyl)tin (1.0g, $2.22 \times 10^{-3}$ moles) and tin(IV) chloride (0.08 $cm^3$, $7.81 \times 10^{-4}$ moles) were heated together, with stirring, in one half of a Schlenk tube. The temperature of the reaction was controlled using an oil bath at 110° C. On cooling, a solid product crystallised out. This material was subsequently dissolved in toluene and filtered into the second half of the Schlenk tube. Reduction of the solvent bulk afforded crystals of the solid product. The supernatant liquid was removed via filtration and the white crystals washed with pure hexane. The product was then redissolved in toluene and filtered into a toluene solution of triphenylphosphine oxide (0.4g, $1.44 \times 10^{-3}$) to yield 0.33g of a white crystalline material, m.p. 157-158°. Anal: Found: C, 55.29; H, 3.75; Cl, 4.91; $C_{30}H_{24}ClOPS_3Sn$ requires: C, 52.85; H, 3.55; Cl, 5.20%.

### b) Tri(2-thienyl)tin Bromide - $Ph_3PO$

Tri(2-thienyl)tin bromide was prepared by a redistribution reaction between tetra(2-thienyl)tin (1.0g, 2.22 $\times 10^{-3}$ moles) and stannic bromide (0.32g, $7.3 \times 10^{-4}$ moles) in one half of a Schlenk tube as described above. The crude product was dissolved in toluene, the solution filtered and then the solid recovered from a toluene/hexane solution on the other side of the Schlenk tube. The organotin halide was then added in toluene solution to triphenylphosphine oxide, also in toluene, to yield a white precipitate, m.p. 144.5-147°.

Anal. Found: C, 51.44; H, 3.45; S, 11.75; $C_{30}H_{24}BrOPS_3Sn$ requires C, 49.61; H, 3.33; S, 13.25%.

## Preparation of Diheteroaryltin Dihalides and their Chemical Characterisation

### Di-(3-thienyl)tin dichloride - 2,2' -bipyridyl complex

Tetra-(3-thienyl)tin (1.0 g, 2.22 x $10^{-3}$ mole) and tin(IV) chloride (0.25 $cm^3$, 2.22 x $10^{-3}$ mole) were heated together with stirring at an oil bath temperature of $85^o$ for 1½ hr. The resulting liquid was dissolved in a mixture of chloroform and toluene (1:1 v/v), to which was added with stirring a similar solution of 2,2' -bipyridyl (0.69 g). The resulting solution rapidly deposited a white solid, which was filtered, washed with toluene and dried. m.p. $242^o$. Anal. Found: C, 42.60; H, 2.80; N, 5.25. $C_{18}H_{14}Cl_2N_2S_2Sn$ requires C, 42.20; H, 2.75; N, 5.45%.

### Di-(3-thienyl)tin dibromide - 2,2' -bipyridyl complex

Tetra-(3-thienyl)tin (1.0 g, 2.22 x $10^{-3}$ mole) and tin(IV) bromide (0.97 g, 2.21 x $10^{-3}$ mole) were heated together with stirring at an oil bath temperature of $90^o$ for 2 hr. The resulting liquid was dissolved in toluene and treated with a toluene solution of 2,2' -bipyridyl (1.38 g) to give the complex, m.p. $253^o$d. Anal. Found: C, 35.65; H, 2.30; N, 4.45. $C_{18}H_{14}Br_2N_2S_2Sn$ requires C, 35.95; H, 2.35; N, 4.65%.

Di-(3-thienyl)tin diiodide A mixture of 3-iodothiophen, (10 g, 4.76 x $10^{-2}$ mole), alkali-washed, powdered tin (2.82 g, 2.38 x $10^{-2}$ mole) and pyridine hydrochloride (0.06 g) was heated together under nitrogen with stirring overnight at an oil bath temperature of 150°. The resulting deep yellow liquid was distilled under reduced pressure to give a fraction, b.p. 200-220° at 0.05 mm Hg, which crystallised on cooling.

TLC analysis indicated the presence of both tetra-(3-thienyl)tin and a diorganotin dihalide. The Mössbauer spectrum of the mixture was also indicative of the presence of tetra-(3-thienyl)tin, and the parameters for di-(3-thienyl)tin diiodide were obtained from computer fits to the combined data.

Di-(3-thienyl)(di-p-tolyl)stannane Di-(3-thienyl)tin dichloride (from the reaction of tetra-(3-thienyl)tin (1.0 g, 2.22 x $10^{-3}$ moles and tin(IV)chloride (0.25 $cm^3$, 2.17 x $10^{-3}$ moles)), dissolved in THF (8 $cm^3$) was treated with the Grignard reagent derived from *p*-bromotoluene (1.48 g, 8.65 x $10^{-3}$ moles) and magnesium (0.25 g, 1.03 x $10^{-2}$ moles) in THF (10 $cm^3$), and the resulting mixture stirred overnight. Treatment of the reaction mixture with aqueous ammonium chloride solution gave a white solid, which was dissolved by the addition of chloroform. Separation of the organic layer, followed by drying over anhydrous magnesium sulphate, and evaporation gave the stannane, m.p. 148-150°, from isopropanol.

Anal: C, 56.3; H, 4.35; S,13.85; $C_{22}H_{20}S_2Sn$ requires C, 56.55; H, 4.30; S, 13.70% $^1H$ n.m.r. ($CDCl_3$): $\delta$ 7.1 - 7.9, (m, 14 Ar H); 2.35, (s, 6H) p.p.m.

### Di(3-furyl)tin dichloride 2,2' - bipyridyl complex

Tetra(3-furyl)tin (0.5g, 1.29 x $10^{-3}$ moles) and tin(IV) chloride (0.15 ml, 1.29 x $10^{-3}$ moles) were heated together, with stirring, at an oil bath temperature of 110° C for 1½ hrs. The resulting liquid was dissolved in toluene, filtered and treated with a toluene solution of 2,2' - bipyridyl (0.4g, 2.56 x $10^{-3}$ moles) to give 0.55g of an insoluble complex, m.pt. 255° C d.

Found : C, 45.10; H, 3.00; N, 5.85; $C_{18}H_{14}Cl_2N_2O_2Sn$ requires C, 45.05; H, 2.95; N, 5.85%.

### Di(3-furyl)tin dibromide 2,2' -bipyridyl complex

Tetra(3-furyl)tin (0.5g, 1.29 x $10^{-3}$ moles) and tin(IV) bromide (0.56g, 1.28 x $10^{-3}$ moles) were heated together, with stirring, at an oil bath temperature of 110° C for 2 hrs. The resulting liquid was dissolved in toluene,

filtered and treated with a toluene solution of 2,2' -bipyridyl (0.4g, 2.56 x $10^{-3}$ moles) to yield an insoluble white complex (0.81g), m.pt. 230° C d.
Found : C, 37.40; H, 2.50; N, 4.90; $C_{18}H_{14}Br_2N_2O_2Sn$ requires C, 38.00; H, 2.50; N, 4.90%.

Di(2-thienyl)tin dichloride 2,2'-bipyridyl complex

Tetra(2-thienyl)tin (1.0g, 2.22 x $10^{-3}$ moles) and tin(IV) chloride (0.25 ml, 2.17 x $10^{-3}$ moles) were heated together, with stirring, at an oil bath temperature of 100° C for 1½ hrs. The liquid product was dissolved in toluene and filtered, in a nitrogen atmosphere, into a toluene solution of the 2,2' -bipyridyl ligand (0.68g, 4.35 x $10^{-3}$ moles) to form a finely divided insoluble complex, m.pt. 240° C d. Found : C, 42.00; H, 2.90; N, 5.25; $C_{18}H_{14}Cl_2N_2S_2Sn$ requires C, 42.20; H, 2.75; N, 5.45%.

Di-(2-thienyl)tin dibromide 2,2'-bipyridyl complex

Tetra(2-thienyl)tin (1.0g, 2.22 x $10^{-3}$ moles) and tin(IV) bromide (0.97g, 2.21 x $10^{-3}$ moles) were melted together, with stirring, at an oil bath temperature of 120°C for 1 hr. A viscous oil was produced. This was subsequently dissolved in hexane and filtered, under nitrogen, into a hexane solution of 2,2'-bipyridyl (0.69g, 4.42 x $10^{-3}$ moles). A dense white precipitate formed almost immediately m.p. 250° C d. Anal. Found : C, 37.13; H, 2.46;

N, 4.25; $C_{18}H_{14}Br_2N_2S_2Sn$ requires C, 35.98; H, 2.35; N,4.66%.

## Di(2-thienyl)tin diiodide

A sample of powdered tin (5.9g, $4.97 \times 10^{-2}$ moles), previously washed with aqueous sodium hydroxide (10% w/v), distilled water and dried, was treated with 2-iodothiophene (21g, 0.1 moles) in the presence of a catalytic amount of pyridine hydrochloride (0.12g, $1.04 \times 10^{-3}$ moles). The reaction was conducted in the absence of a solvent at $150^{o}$ with vigorous stirring. The reaction mixture became reddish in colour and after 2½ hrs was allowed to cool. After filtration, purification of the crude product was attempted *via* vacuum distillation using an air condenser. Initially, some unreacted iodothiophen was recovered, followed by a yellow oil. However, a high boiling impurity co-distilled with this oil, which crystallised on cooling. The Mössbauer spectrum of the distillate revealed a singlet due to tetra(2-thienyl)tin as well as the expected doublet for the di(2-thienyl)tin diiodide. Further evidence for the disproportionation of the di-(2-thienyl)tin diiodide was provided from the orange residue of tin(IV)iodide on the distillation apparatus.

## Di-(2-thienyl)tin diiodide 2,2'-bipyridyl complex

Equimolar quantities of tetra-(2-thienyl)tin (0.5g) and tin(IV) iodide (0.69g) were heated together, with stirring and in the presence of a nitrogen atmosphere, for 2 hrs at an oil bath temperature of 125° C. This yielded an orange/brown oil which was dissolved in toluene and treated with 2,2'- bipyridyl (0.34g, 2.18 x $10^{-3}$ moles), also in toluene solution. A finely-divided orange precipitate was produced, m.p. 200° C d.

Anal. Found: C, 29.88; H, 1.96; N, 3.86; $C_{18}H_{14}I_2N_2S_2Sn$ requires C, 31.11; H, 2.03; N, 4.03%.

<u>Di-(2-furyl)tin dichloride 1,10-phenanthroline complex</u>

Tetra-(2-furyl)tin (1.0g, 2.59 x $10^{-3}$ moles) and tin(IV) chloride (0.3cm$^3$, 2.60 x $10^{-3}$ moles) were heated together, with mixing at 100° C. The resultant viscous liquid was dissolved in toluene and treated with a similar solution of 1,10-phenanthroline (0.9g, 4.99 x $10^{-3}$ moles) A finely divided precipitate was quickly formed, filtered and dried, m.p. 250° C d. Anal. Found: C, 45.91; H, 2.66; N, 5.22: $C_{20}H_{14}Cl_2N_2O_2Sn$ requires C, 47.67; H, 2.80; N, 5.56%.

<u>Di(2-furyl)tin dibromide 2,2'-bipyridyl complex</u>

(i) Tetra(2-furyl)tin (0.5g, 1.29 x $10^{-3}$ moles) and tin (IV)bromide (0.56g, 1.28 x $10^{-3}$ moles) were heated together, with stirring, for ¾ hr. 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 (0.4g, 2.56 x $10^{-3}$ moles) resulting in the immediate formation of a dense white precipitate, m.p. 200° C d.

Found: C, 37.10; H, 2.30; N, 4.80: $C_{18}H_{14}Br_2N_2O_2Sn$ requires C, 38.00; H, 2.50; N, 4.90%.

(ii) Tetra(2-furyl)tin (0.5g, 1.29 x $10^{-3}$ moles) and tin(IV)bromide (0.19g, 4.33 x $10^{-4}$ moles) were heated together, with stirring, at an oil bath temperature of 80° C for 1 hr. 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 (0.13g, 8.32 x $10^{-4}$ moles), a finely divided white precipitate was quickly formed, m.pt. 236° C d.

Found: C, 38.50; H, 2.55; N, 5.05; $C_{18}H_{14}Br_2N_2O_2Sn$ requires C, 38.00; H, 2.50; N, 4.90%.

Di-(2-furyl)tin diiodide 2,2'-bipyridyl complex

Tetra(2-furyl)tin (0.5g, 1.29 x $10^{-3}$ moles) and tin(IV) iodide (0.81g, 1.29 x $10^{-3}$ moles) were heated together, with stirring; the resultant liquid was taken up in toluene and treated with a toluene solution of 2,2'- bipyridyl, producing a finely divided orange precipitate which decomposed at high temperature.

Anal. Found: C, 31.09; H, 2.03; N, 4.10: $C_{18}H_{14}I_2N_2O_2Sn$ requires C, 32.62; H, 2.13; N, 4.23%.

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# CHAPTER 3: CRYSTAL AND MOLECULAR STRUCTURE OF TRI-3-THIENYLTIN BROMIDE AND A TRIPHENYLPHOSPHINE OXIDE ADDUCT

## 3.1 Introduction

Mössbauer results obtained for the triheteroaryltin halides (see Chapter 2, section 2) are indicative of four coordinate unassociated tin, suggesting that there is little interaction between ring heteroatoms and tin from adjacent molecules. This is perhaps rather surprising in view of the tendency for triorganotin halides to become five-coordinate in the presence of a suitable donor ligand[1]. The possible electron-withdrawing properties of the heteroaryl groups may result in the tin being more electropositive and therefore more susceptible to coordination, potential donors being either the ring heteroatom or the covalently bound halogen from a neighbouring molecule. In order to resolve this point, the solid state structure of tri(3-thienyl)tin bromide has been investigated by single crystal X-ray analysis. A preliminary study, discussed herein, shows the molecule to be extensively disordered and detailed structural data have not been obtained. The triphenylphosphine oxide (TPPO) adduct of tri(3-thienyl)tin bromide has also been prepared. X-ray crystallographic data are presented and show the rotational disordere inherent in the parent molecule to be considerably reduced upon complex formation.

## 3.2 Experimental

### 3.2.1 Preparative

Tri(3-thienyl)tin bromide and its triphenylphosphine oxide adduct were prepared as described in section 2.4. Density measurements were made using aqueous potassium iodide.

### 3.2.2 Crystal Data

#### A. Tri(3-thienyl)tin bromide

$C_{12}H_9BrS_3Sn$, Mr = 448.0, monoclinic, space group C2, a = 15.071(15), b = 11.416(11), c = 9.403(10) Å. β = 109.84(7)°, V = 1521.8 Å$^3$, Z = 4, Dc = 1.96 Mgm$^{-3}$, Dm = 1.93 Mgm$^{-3}$, μ (Mo - K$_\alpha$) = 4.49 mm$^{-1}$, F(000) = 856.

#### B. Tri(3-thienyl)tin bromide . triphenylphosphine oxide

$C_{30}H_{24}BrOPS_3Sn$, Mr = 726.7, triclinic, space group P$\bar{1}$, a = 14.700(10), b = 11.002(8), c = 9.805(7) Å, α = 104.05(6), β = 95.04(5), γ = 101.71(5)°, V = 1490.5 Å$^3$, Z = 2, Dc = 1.62 Mgm$^{-3}$, Dm = 1.58 Mgm$^{-3}$, μ (Mo - K$_\alpha$ ) = 2.36. mm$^{-1}$, F(000) = 720.

### 3.2.3 Data Collection and Reduction

#### A. Tri(3-thienyl)tin bromide

A crystal, approximate dimensions 0.20 x 0.28 x 0.30 mm was selected and mounted with the c-axis coincident with the rotation (ω) axis of a Stöe Stadi-2 two circle diffractometer. With monochromated M$_O$ - K$_\alpha$ radiation and using the background-ω scan-background technique, 1762 unique reflections were measured, of which 1604 had I > 3.0 σ (I) and were considered to be observed. Corrections for Lorentz and polarisation effects were applied to the data, but no corrections for absorption were made.

#### B. Tri(3-thienyl)tin bromide . triphenylphosphine oxide

Intensities were measured for a crystal, approximate dimensions 0.10 x 0.18 x 0.38 mm, mounted on a glass fibre with the c-axis coincident with the ω-axis of a Stöe-Stadi-2 two circle diffractometer. Monochromatic $M_o$ - $K_\alpha$ radiation was used and the background-$\omega$ scan-background technique employed to give 4989 independent reflections, of which 4375 had $I > 3\sigma(I)$ and were used for subsequent analysis. Corrections were applied as above.

### 3.2.4 Structure Determination and Refinement

#### A. Tri(3-thienyl)tin bromide

Systematic absences do not distinguish between the space groups C2 and C2/m. Density measurements indicate Z = 4 which for the space group C2/m would require the molecule to have mirror symmetry. In the non-centrosymmetric space groups, C2, the molecule would occupy a general position and subsequent analysis confirms this space group to be correct. The approximate positions of the tin and bromine atoms were calculated using a three-dimensional Patterson synthesis. Successive difference Fourier maps revealed the three thienyl groups to be extensively disordered with rotational disorder about the Sn-Br bond (approximately $26^{\circ}$, Fig. 3.1) and also about each of the Sn-C (thienyl) bonds, approximately $180^{\circ}$. This disorder results in two probable ring sites containing three possible positions for each of the sulphur atoms. Attempts to fit ideal geometry to the thienyl groups met with only very limited success and the structure could only be refined to R = 0.135. Bond distances and angles about tin are given, in relation to one of each pair of thienyl rings, in table 3.1.

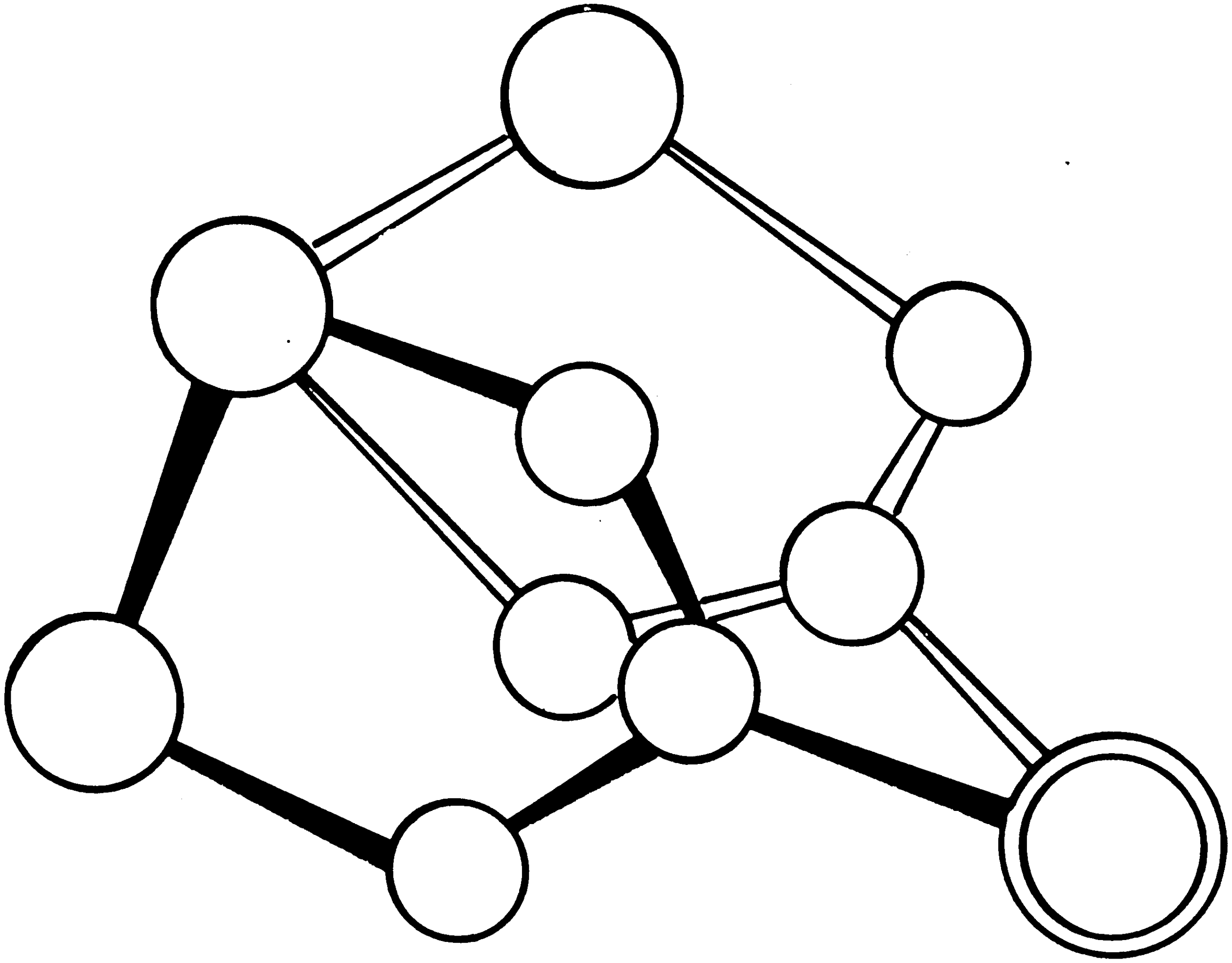

Fig. 3.1

**ROTATIONAL DISORDER ; TRI(3-THIENYL)TIN BROMIDE**

Table 3.1

Selected bond distances (Å) and angles (°) in tri(3-thienyl)-tin bromide, with estimated standard deviations in parentheses.

(a) Distances (Å)

| | |
|---|---|
| Sn-Br | 2.490(7) |
| Sn-C11 | 2.02(6) |
| Sn-C12 | 2.07(5) |
| Sn-C13 | 2.08(4) |

(b) Angles (°)

| | |
|---|---|
| Br-Sn-C11 | 105.8(1.8) |
| Br-Sn-C12 | 106.4(1.6) |
| Br-Sn-C13 | 103.0(1.5) |
| C11-Sn-C12 | 115.1(2.3) |
| C11-Sn-C13 | 108.0(2.1) |
| C12-Sn-C13 | 117.1(1.7) |

### B. Tri(3-thienyl)tin bromide - triphenylphosphine oxide

Preliminary photographs showed the crystal to be triclinic and subsequent analysis confirmed the space group to be $P\bar{1}$. The approximate positions of the tin and bromine atoms were calculated from a three-dimensional Patterson synthesis and the remaining atoms were located from successive difference Fourier maps. While one of the 3-thienyl groups is ordered, the other two contain rotational disorder such that two thienyl groups (having approximately 50% occupancy) are related to each other by a pseudo two-fold axis about the Sn-C(n1) (n = 4,6) bonds. Each of the disordered 3-thienyl entities were given ideal geometries and included in the least squares refinement with common isotropic temperature factors applied to atoms related by the pseudo symmetry. The population parameters applied to each pair of thienyl units were refined, the final values corresponding to occupancies of 55 and 45% for the C(n1), C(n2A), S(n3A), C(n4A), C(n5A) and C(n1), C(n2B), S(n3B), C(n4B), C(n5B) moieties respectively. Hydrogen atoms were located for the three phenyl and ordered 3-thienyl groups, but given ideal geometry (C-H 1.08 Å). Common isotropic temperature factors were applied to phenyl hydrogens and also to thienyl hydrogens, which refined to final values of $\underline{U} = 0.088(9), 0.081(13)$ $Å^2$ respectively. Scattering factors were calculated using an analytical approximation[2] and the weighting scheme $w = 0.956 / [\sigma^2 (\underline{Fo}) + 0.006 (\underline{Fo})^2]$ adopted. All ordered non-hydrogen atoms were given anisotropic temperature factors and refinement converged at R = 0.055, R' = 0.067. Final positional parameters are given in Table 3.2, bond distances and angles in Table 3.3. The labelling scheme adopted is shown in Fig. 3.2. Lists of structure factors, thermal parameters and mean planes data can be found in Tables 3.4, 3.5 and 3.6 respectively.

## 3.3 Discussion

Although it has not proved possible to gain detailed structural data for tri(3-thienyl)tin bromide, it has been established that the tin atom occupies a tetrahedral environment (Table 3.1) in which the three thienyl rings exhibit a characteristic propeller geometry. As suggested on consideration of Mössbauer data, there is no evidence of any intermolecular tin-sulphur or tin-halogen interactions.

The TPPO adducts of triphenyltin halides have been predicted, on the basis of partial quadrupole splitting calculations[3,4] to have a trigonal bipyramidal structure with equatorial aryl groups. The observation of similar Mössbauer parameters for the related (3-thienyl) compounds (Table 3.7) suggests that they also adopt a similar geometry. $^{119}$Sn n.m.r. solution studies (see Chapter 2, section 3) are also indicative of an increase in coordination number for tin. The $^{119}$Sn n.m.r. signal shifts to a considerably lower frequency for the adduct compared with the unassociated tin species.

The present single crystal X-ray study confirms that the TPPO adduct of tri(3-thienyl)tin bromide does adopt a trigonal bipyramidal arrangement in the solid state, in which bromine and oxygen (triphenylphosphine oxide) occupy

### Table 3.2

Final Positional Parameters (x $10^5$ for Sn and x $10^4$ for other atoms) with estimated standard deviations in parentheses*

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Sn | 27036(3) | 44611(4) | 20342(4) |
| Br | 3314(1) | 2338(1) | 1139(1) |
| P | 2349(1) | 7775(1) | 2983(1) |
| O | 2174(3) | 6341(3) | 2805(4) |
| C(11) | 2381(4) | 8601(5) | 4818(6) |
| C(12) | 2425(4) | 7924(6) | 5828(6) |
| C(13) | 2406(5) | 8531(8) | 7230(7) |
| C(14) | 2366(5) | 9791(8) | 7622(8) |
| C(15) | 2327(6) | 10454(7) | 6650(10) |
| C(16) | 2343(5) | 9905(6) | 5216(8) |
| C(21) | 3422(4) | 8402(5) | 2371(6) |
| C(22) | 4122(4) | 9421(6) | 3242(7) |
| C(23) | 4936(5) | 9825(7) | 2716(8) |
| C(24) | 5075(5) | 9242(8) | 1351(8) |
| C(25) | 4379(5) | 8257(7) | 506(7) |
| C(26) | 3551(4) | 7834(6) | 1018(7) |
| C(31) | 1381(4) | 8139(5) | 2018(6) |
| C(32) | 1445(5) | 8587(7) | 825(7) |
| C(33) | 625(7) | 8715(9) | 51(9) |
| C(34) | -232(6) | 8372(8) | 459(9) |
| C(35) | -277(5) | 8012(7) | 1692(10) |
| C(36) | 520(4) | 7873(7) | 2476(8) |
| C(41) | 1640 | 3608 | 3070 |
| C(42A) | 1060 | 4292 | 3766 |
| S(43A) | 169 | 3246 | 4207 |
| C(44A) | 699 | 1990 | 3796 |
| C(45A) | 1480 | 2305 | 3193 |
| C(42B) | 1698 | 2556 | 3556 |
| S(43B) | 615 | 1927 | 3955 |
| C(44B) | 247 | 3309 | 4017 |
| C(45B) | 868 | 4145 | 3526 |
| C(51) | 3997(4) | 5578(5) | 3262(6) |
| C(52) | 4771(5) | 6023(8) | 2722(9) |
| S(53) | 5666(2) | 6941(2) | 3996(4) |
| C(54) | 5059(6) | 6778(7) | 5251(9) |
| C(55) | 4157(5) | 5999(6) | 4764(7) |
| C(61) | 2297 | 4590 | -50 |
| C(62A) | 2762 | 4177 | -1156 |
| S(63A) | 2293 | 4550 | -2633 |
| C(64A) | 1396 | 5047 | -1843 |
| C(65A) | 1488 | 5055 | -454 |
| C(62B) | 1760 | 5419 | -292 |
| S(63B) | 1407 | 5096 | -2088 |
| C(64B) | 2437 | 4658 | -2366 |
| C(65B) | 2769 | 4234 | -1252 |

| | | | |
|---|---|---|---|
| H(12) | 2447 | 6920 | 5508 |
| H(13) | 2451 | 8018 | 8034 |
| H(14) | 2326 | 10259 | 8712 |
| H(15) | 2322 | 11463 | 6985 |
| H(16) | 2305 | 10444 | 4435 |
| H(22) | 4026 | 9873 | 4310 |
| H(23) | 5471 | 10628 | 3374 |
| H(24) | 5732 | 9540 | 977 |
| H(25) | 4465 | 7824 | -574 |
| H(26) | 3008 | 7044 | 356 |
| H(32) | 2117 | 8809 | 463 |
| H(33) | 676 | 9069 | -881 |
| H(34) | -851 | 8468 | -146 |
| H(35) | -952 | 7812 | 2052 |
| H(36) | 465 | 7534 | 3418 |
| H(52) | 4833 | 5794 | 1604 |
| H(54) | 5317 | 7248 | 6359 |
| H(55) | 3656 | 5736 | 5444 |

*Two of the three (3-thienyl) groups are disordered. The first is comprised of C(41), C(42A), S(43A), C(44A), C(45A) and C(41), C(42B), S(43B), C(44B), C(45B) rings and the second of C(61), C(62A), S(63A), C(64A), C(65A) and C(61), C(62B), S(63B), C(64B), C(65B).

## Table 3.3

Bond distances (Å) and bond angles (°) with estimated standard deviations for ordered atoms in parentheses.

### Distances (Å)

| | | | |
|---|---|---|---|
| Sn-Br | 2.651(1) | P-O | 1.510(4) |
| Sn-O | 2.335(4) | P-C(11) | 1.799(5) |
| Sn-C(41) | 2.121 | P-C(21) | 1.803(6) |
| Sn-C(51) | 2.122(5) | P-C(31) | 1.805(6) |
| Sn-C(61) | 2.125 | | |

| | | | |
|---|---|---|---|
| C(41)-C(42A) | 1.369 | C(41)-C(42B) | 1.369 |
| C(42A)-S(43A) | 1.720 | C(42B)-S(43B) | 1.720 |
| S(43A)-C(44A) | 1.703 | S(43B)-C(44B) | 1.704 |
| C(44A)-C(45A) | 1.359 | C(44B)-C(45B) | 1.365 |
| C(45A)-C(41) | 1.441 | C(45B)-C(41) | 1.439 |

| | |
|---|---|
| C(51)-C(52) | 1.349(10) |
| C(52)-S(53) | 1.694(7) |
| S(53)-C(54) | 1.606(10) |
| C(54)-C(55) | 1.396(10) |
| C(55)-C(51) | 1.416(8) |

| | | | |
|---|---|---|---|
| C(61)-C(62A) | 1.366 | C(61)-C(62B) | 1.369 |
| C(62A)-S(63A) | 1.723 | C(62B)-S(63B) | 1.719 |
| S(63A)-C(64A) | 1.704 | S(63B)-C(64B) | 1.704 |
| C(64A)-C(65A) | 1.355 | C(64B)-C(65B) | 1.377 |
| C(65A)-C(61) | 1.446 | C(65B)-C(61) | 1.433 |

| | n = 1 | n = 2 | n = 3 |
|---|---|---|---|
| C(n1)-C(n2) | 1.381(9) | 1.399(7) | 1.379(10) |
| C(n2)-C(n3) | 1.381(9) | 1.379(10) | 1.417(12) |
| C(n3)-C(n4) | 1.360(12) | 1.388(11) | 1.362(13) |
| C(n4)-C(n5) | 1.338(13) | 1.369(9) | 1.363(14) |
| C(n5)-C(n6) | 1.393(11) | 1.393(10) | 1.400(11) |
| C(n6)-C(n1) | 1.407(9) | 1.370(8) | 1.379(9) |

### Bond Angles (°)

| | | | |
|---|---|---|---|
| Br-Sn-O | 179.4(1) | C(51)-Sn-C(61) | 121.5(2) |
| Br-Sn-C(41) | 95.1 | P-O-Sn | 146.9(2) |
| Br-Sn-C(51) | 95.6(2) | O-P-C(11) | 110.0(3) |
| Br-Sn-C(61) | 94.0 | O-P-C(21) | 112.4(2) |
| O-Sn-C(41) | 85.5 | O-P-C(31) | 109.8(2) |
| O-Sn-C(51) | 84.3(2) | C(11)-P-C(21) | 109.7(2) |
| O-Sn-C(61) | 85.5 | C(11)-P-C(31) | 105.8(3) |
| C(41)-Sn-C(51) | 119.0(2) | C(21)-P-C(31) | 108.9(3) |
| C(41)-Sn-C(61) | 117.4 | | |

|  |  |  |  |
|---|---|---|---|
| Sn-C(41)-C(42A) | 121.9 | Sn-C(41)-C(42B) | 122.0 |
| Sn-C(41)-C(45A) | 125.0 | Sn-C(41)-C(45B) | 125.3 |
| C(42A)-C(41)-C(45A) | 112.9 | C(42B)-C(41)-C(45B) | 112.1 |
| C(41)-C(42A)-S(43A) | 109.1 | C(41)-C(42B)-S(43B) | 108.4 |
| C(42A)-S(43A)-C(44A) | 93.3 | C(42B)-S(43B)-C(44B) | 92.8 |
| S(43A)-C(44A)-C(45A) | 111.2 | S(43B)-C(44B)-C(45B) | 111.0 |
| C(41)-C(45A)-C(44A) | 111.9 | C(41)-C(45B)-C(44B) | 111.5 |

|  |  |
|---|---|
| Sn-C(51)-C(52) | 124.9(5) |
| Sn-C(51)-C(55) | 124.6(4) |
| C(52)-C(51)-C(55) | 110.4(5) |
| C(51)-C(52)-S(53) | 112.8(6) |
| C(52)-S(53)-C(54) | 92.5(4) |
| S(53)-C(54)-C(55) | 113.3(6) |
| C(51)-C(55)-C(54) | 110.9(6) |

|  |  |  |  |
|---|---|---|---|
| Sn-C(61)-C(62A) | 122.2 | Sn-C(61)-C(62B) | 121.6 |
| Sn-C(61)-C(65A) | 124.1 | Sn-C(61)-C(65B) | 125.7 |
| C(62A)-C(61)-C(65A) | 113.7 | C(62B)-C(61)-C(65B) | 109.3 |
| C(61)-C(62A)-S(63A) | 108.9 | C(61)-C(62B)-S(63B) | 109.3 |
| C(62A)-S(63A)-C(64A) | 93.8 | C(62B)-S(63B)-C(64B) | 88.4 |
| S(63A)-C(64A)-C(65A) | 111.2 | S(63B)-C(64B)-C(65B) | 110.5 |
| C(61)-C(65A)-C(64A) | 111.8 | C(61)-C(65B)-C(64B) | 110.9 |

|  | n = 1 | n = 2 | n = 3 |
|---|---|---|---|
| P-C(n1)-C(n2) | 118.8(4) | 122.0(5) | 124.1(5) |
| P-C(n1)-C(n6) | 120.7(5) | 118.1(4) | 116.6(5) |
| C(n2)-C(n1)-C(n6) | 120.5(5) | 119.9(5) | 119.2(6) |
| C(n1)-C(n2)-C(n3) | 119.2(6) | 118.8(6) | 119.9(7) |
| C(n2)-C(n3)-C(n4) | 120.5(8) | 121.5(6) | 120.5(9) |
| C(n3)-C(n4)-C(n5) | 120.5(7) | 119.0(7) | 118.9(8) |
| C(n4)-C(n5)-C(n6) | 122.1(7) | 120.4(6) | 121.7(7) |
| C(n1)-C(n6)-C(n5) | 117.0(7) | 120.4(5) | 119.5(7) |

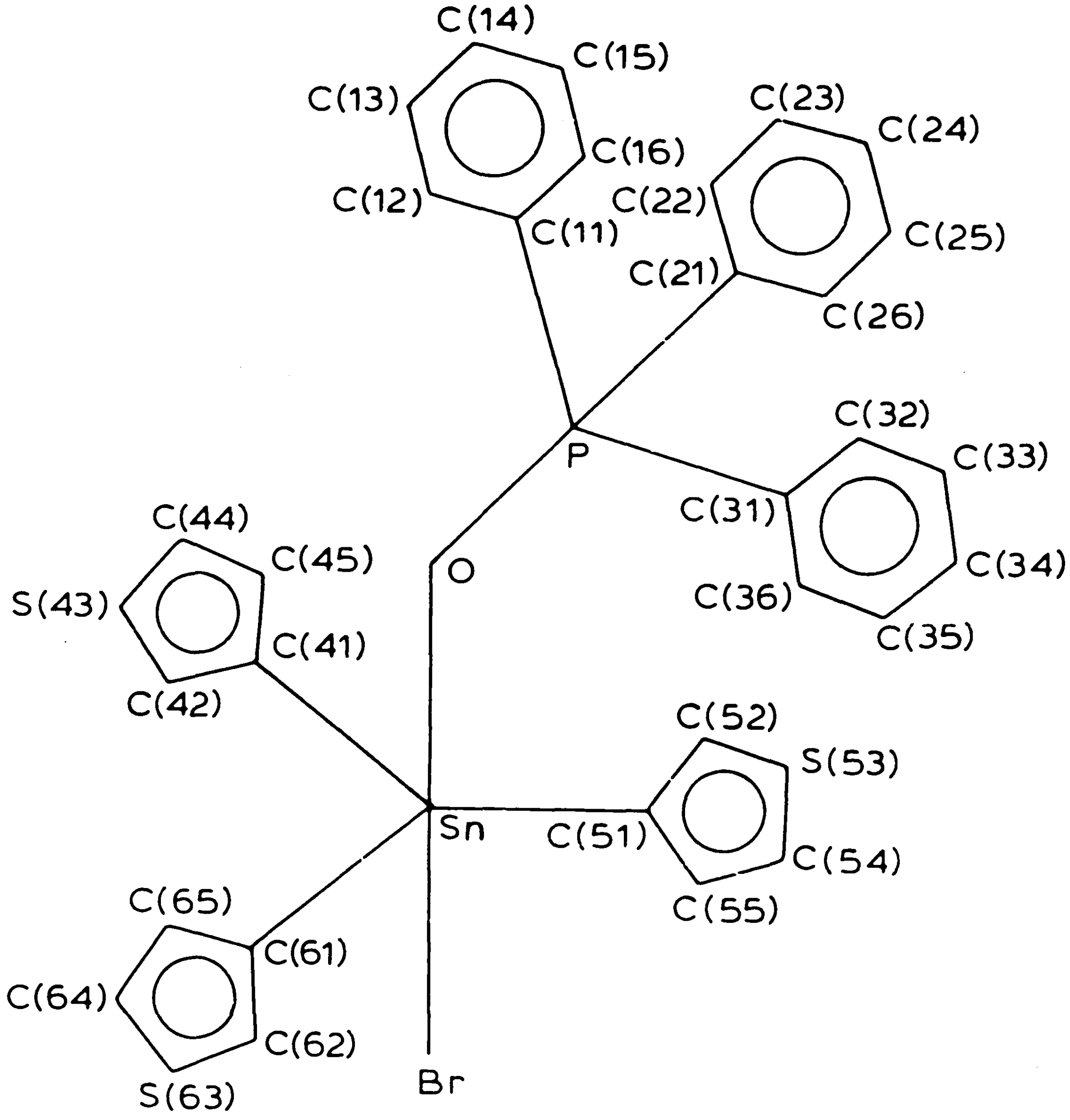

**Fig. 3.2**

**Labelling Scheme Adopted for Tri-3-thienyltin Bromide . Triphenylphosphine Oxide**

Table 3.4

Final thermal parameters for non-hydrogen atoms with estimated standard deviations in parentheses

(a) Anisotropic temperature factors (x $10^4$) in the form

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Sn | 411(2) | 415(2) | 363(2) | 0(2) | 16(2) | 114(2) |
| Br | 793(5) | 635(4) | 688(5) | -160(4) | -47(4) | 395(4) |
| P | 413(7) | 332(6) | 357(7) | 64(5) | 97(5) | 97(5) |
| O | 451(20) | 328(18) | 464(21) | 54(16) | 125(16) | 101(15) |
| C(11) | 441(27) | 383(27) | 405(28) | 60(23) | 108(22) | 126(22) |
| C(12) | 600(35) | 521(33) | 448(31) | 135(27) | 52(27) | 62(27) |
| C(13) | 731(44) | 849(52) | 372(32) | 62(34) | 121(30) | 0(37) |
| C(14) | 711(44) | 772(50) | 519(40) | -120(38) | 184(34) | -42(36) |
| C(15) | 809(49) | 529(39) | 919(59) | -199(41) | 301(44) | 126(35) |
| C(16) | 856(47) | 379(31) | 694(43) | -63(30) | 207(36) | 139(30) |
| C(21) | 472(29) | 405(27) | 415(28) | 115(24) | 137(23) | 92(22) |
| C(22) | 511(33) | 615(38) | 583(37) | 159(32) | 94(28) | 24(28) |
| C(23) | 504(35) | 738(45) | 713(44) | 217(38) | 73(31) | -55(31) |
| C(24) | 553(37) | 871(51) | 757(49) | 351(43) | 216(34) | 116(35) |
| C(25) | 602(38) | 725(43) | 610(39) | 211(35) | 277(32) | 135(33) |
| C(26) | 533(33) | 568(34) | 532(35) | 114(29) | 156(27) | 11(27) |
| C(31) | 453(28) | 350(25) | 426(28) | 106(23) | 57(22) | 81(21) |
| C(32) | 656(39) | 856(47) | 642(40) | 410(38) | 237(32) | 357(36) |
| C(33) | 935(60) | 950(63) | 763(52) | 350(49) | -63(44) | 335(49) |
| C(34) | 713(46) | 818(50) | 786(50) | 240(43) | -121(38) | 322(39) |
| C(35) | 482(34) | 702(45) | 1105(61) | 358(45) | 49(36) | 114(31) |
| C(36) | 477(33) | 804(44) | 709(42) | 371(37) | 108(29) | 163(31) |
| C(41) | 532(30) | 402(28) | 395(28) | 40(23) | 3(23) | 91(23) |
| C(51) | 413(27) | 458(29) | 494(31) | 58(25) | -34(23) | 126(22) |
| C(52) | 493(37) | 1032(61) | 890(55) | 323(49) | 47(36) | 25(37) |
| S(53) | 575(11) | 848(15) | 1606(25) | 396(17) | -209(14) | -83(10) |
| C(54) | 989(56) | 598(41) | 744(49) | -200(37) | -403(44) | 351(40) |
| C(55) | 663(39) | 604(38) | 467(33) | -11(29) | -109(29) | 238(31) |
| C(61) | 463(29) | 436(29) | 480(31) | 20(25) | 49(24) | 84(23) |

(b) Isotropic temperature factors (x $10^3$) in the form

$$\exp[-U\sin^2\theta/\lambda^2]$$

| | | | |
|---|---|---|---|
| C(42A),C(42B) | 103(4) | C(62A),C(62B) | 112(5) |
| S(43A),S(43B) | 69(1) | S(63A),S(63B) | 73(1) |
| C(44A),C(44B) | 212(13) | C(64A),C(64B) | 198(12) |
| C(45A),C(45B) | 31(1) | C(65A),C(65B) | 31(2) |

Table 3.5

Deviations (Å) from selected least squares mean planes for tri(3-thienyl)tin bromide triphenylphosphine oxide. Deviations in parentheses are for atoms not included in the calculation of the plane.

---

Plane A

C(11)-C(16)
C(11), 0.007(6); C(12), -0.006(6); C(13), 0.004(8);
C(14), -0.003(8); C(15), 0.004(9); C(16), -0.006(8);
P, [0.075(2)]

Plane B

C(21)-C(26)
C(21), -0.005(6); C(22), 0.002(7); C(23), 0.003(8);
C(24), -0.006(8); C(25), 0.004(8); C(26), 0.002(7);
P, [-0.058(1)]

Plane C

C(31)-C(36)
C(31), 0.024(6); C(32), -0.010(7); C(33), -0.019(10);
C(34), 0.035(9); C(35), -0.021(8); C(36), -0.009(8);
P, [0.214(1)]

Plane D

C(41), C(42A), S(43A), C(44A), C(45A)
C(41), 0.070; C(42A), -0.079; S(43A), 0.057;
C(44A), -0.031; C(45A), -0.016; Sn, [0.291]

Plane E

C(41), C(42B), S(43B), C(44B), C(45B)
C(41), 0.115; C(42B), -0.127; S(43B), 0.087
C(44B), -0.043; C(45B), -0.032; Sn, [0.385]

Plane F

C(61), C(62A), S(63A), C(64A), C(65A)
C(61), -0.036; C(62A), 0.050; S(63A), -0.042;
C(64A), 0.032; C(65A), -0.003; Sn, [-0.113]

Plane G

C(61), C(62B), S(63B), C(64B), C(65B)
C(61), 0.133; C(62B), -0.210; S(63B), +0.188;
C(64B), -0.153; C(65B), 0.043; Sn, [0.091]

### Plane H

C(51), C(52), S(53), C(54), C(55)
C(51), 0.005(6): C(52), 0.000(9); S(53), -0.005(3);
C(54), 0.009(8); C(55), -0.010(7); Sn, [0.095(1)]

### Plane I

C(51), C(61), C(41)
C(51), 0.000; C(61), -0.000; C(41), 0.000;
Sn, [0.182]

### Plane J

Sn, O, P

### Angles (°) between least squares planes

| | | | | | |
|---|---|---|---|---|---|
| A/B | 68.6 | | | | |
| A/C | 79.5 | | | | |
| B/C | 59.2 | | | | |
| A/D | 56.8 | B/D | 58.8 | C/D | 62.0 |
| A/E | 63.4 | B/E | 72.2 | C/E | 48.8 |
| A/F | 51.8 | B/F | 66.5 | C/F | 32.7 |
| A/G | 47.1 | B/G | 69.3 | C/G | 38.0 |
| A/H | 73.4 | B/H | 17.9 | C/H | 42.1 |
| D/E | 14.0 | | | | |
| D/F | 65.0 | E/F | 57.7 | | |
| D/G | 65.5 | E/G | 59.4 | | |
| D/H | 76.3 | E/H | 89.9 | | |
| D/I | 86.7 | E/I | 72.7 | | |
| F/G | 5.4 | | | | |
| F/H | 56.2 | G/H | 60.2 | | |
| F/I | 55.8 | G/I | 60.9 | | |
| H/I | 20.6 | | | | |
| I/J | 89.4 | | | | |

Table 3.6

Least squares planes equations of the form

$aX + bY + cZ - d = 0$

| Plane | a | b | c | d |
|---|---|---|---|---|
| A | -0.9577 | -0.2490 | -0.1440 | -3.7692 |
| B | -0.5314 | 0.7745 | -0.3432 | 4.2024 |
| C | 0.1075 | -0.8301 | -0.5472 | -7.9002 |
| D | -0.4291 | -0.0265 | -0.9029 | -3.3354 |
| E | -0.2719 | -0.2088 | -0.9394 | -3.8382 |
| F | -0.3752 | -0.8888 | -0.2631 | -5.2420 |
| G | -0.4540 | -0.8638 | -0.2185 | -5.4751 |
| H | -0.5147 | 0.8563 | -0.0434 | 2.0397 |
| I | 0.5528 | -0.7760 | -0.3037 | -2.5308 |
| J | -0.4059 | 0.0806 | -0.9103 | -2.5363 |

## Table 3.7

## Mössbauer Data for Tri(3-thienyl), Triphenyltin halides and their Triphenylphosphineoxide Adducts

| | Isomer Shift[a] δ(mm/s ± 0.02) | Quadrupole Splitting Δ(mm/s ± 0.02) |
|---|---|---|
| $Ph_3SnCl$ | 1.37 | 2.45 (Ref 13) |
| $Ph_3SnBr$ | 1.37 | 2.46 |
| $(3\text{-}C_4H_3S)_3SnCl$ | 1.21 | 2.29 |
| $(3\text{-}C_4H_3S)_3SnBr$ | 1.25 | 2.08 |
| | | |
| $Ph_3SnCl.Ph_3P{=}O$ | 1.28 | 3.23 (Ref 3) |
| $Ph_3SnBr.Ph_3P{=}O$ | 1.29 | 3.20 (Ref 3) |
| $(3\text{-}C_4H_3S)_3SnCl.Ph_3P{=}O$ | 1.18 | 3.08 |
| $(3\text{-}C_4H_3S)_3SnBr.Ph_3P{=}O$ | 1.21 | 3.30 |

a Relative to $BaSnO_3$

the axial positions while the heteroaryl groups are equatorial (Fig. 3.3). Although there is only a slight angular distortion from a regular trigonal bipyramidal arrangement, the bond angles do reveal that the tin atom lies out of the trigonal equatorial plane (0. 182 Å), and in a direction towards the bromine atom. Thus the C-Sn-Br angles lie in the range 94.0-95.6°, while the C-Sn-O angles are significantly smaller, ranging from 84.3-85.5°. In general, the structure is reminiscent of an early $S_N2$-like transition state for substitution at tin.

The disordered (3-thienyl) groups show an almost equal preference for the two possible sites with population parameters of 55% and 45%. The apparent ease with which these thienyl units may rotate about the Sn-C bond appears to be a consequence of the lack of any significant inter- and/or intra-molecular interactions involving the heteroaryl group. Rotational disorder of this type has previously been observed for (2-thienyl) groups attached to tin.[5] Similar disorder has been found both for (3-thienyl) and for (2-thienyl) groups attached to phosphorus.[6,7] In contrast, the C(51), C(52), S(53), C(54), C(55) ligand is completely ordered and this may be a direct consequence of the close proximity of one of the phenyl groups, C(21)-C(26), thereby inhibiting rotation about the Sn-C(51) bond.

The Sn-Br distance (2.651(1) Å) is increased relative to that found in the parent tri(3-thienyl)tin bromide molecule (2.49 Å), and is significantly longer than the sum of the covalent radii (2.54 Å). This would appear to reflect an increase in the coordination number of tin, from four to

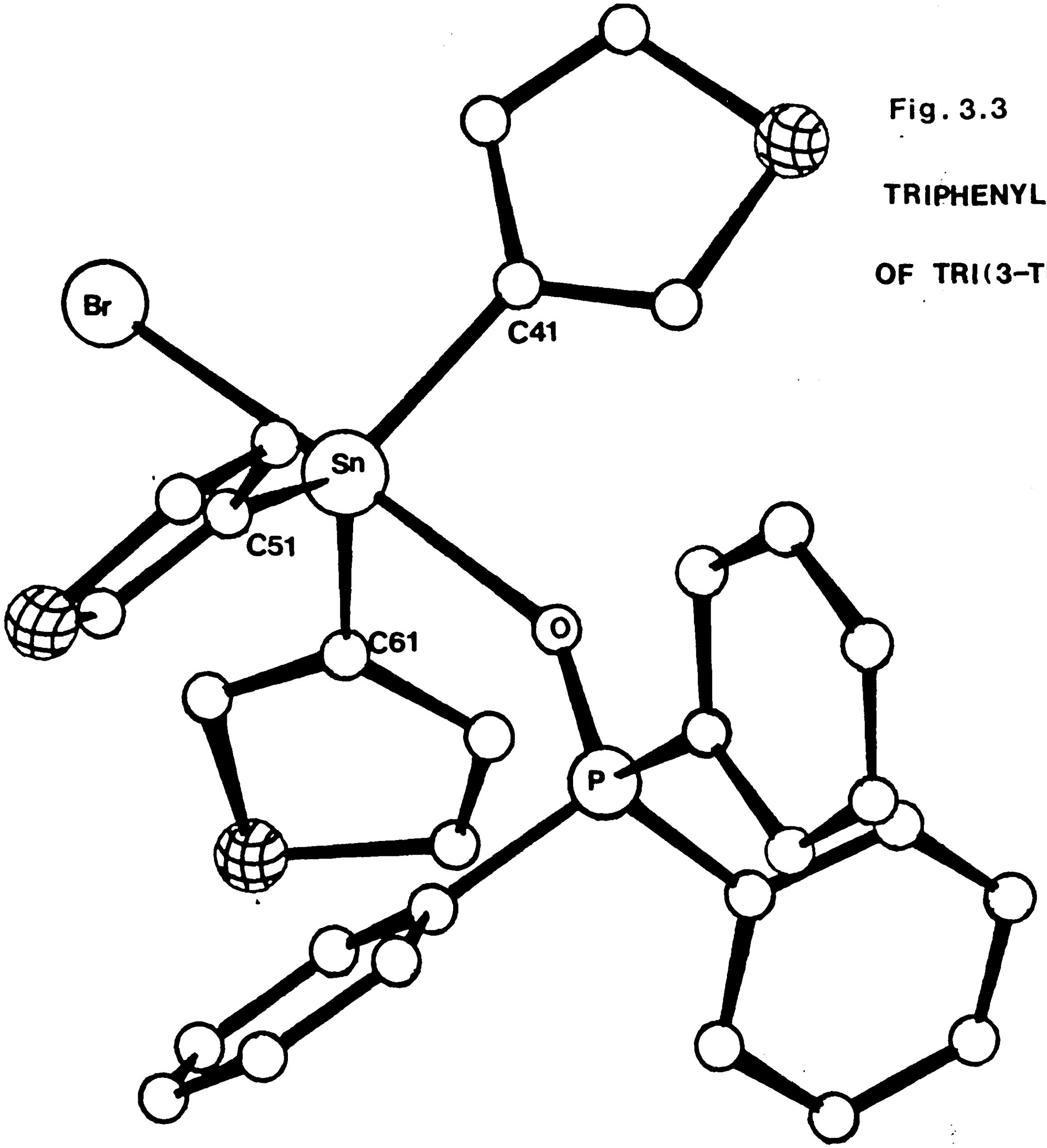

Fig. 3.3

TRIPHENYLPHOSPHINE OXIDE ADDUCT

OF TRI(3-THIENYL)TIN BROMIDE

five. Similar lengthening of the tin-halogen bond has been observed for trimethyltin chloride on complexation with hexamethyltriamido phosphate (from 2.36 to 2.52(2) Å[8]). The length of the Sn-O bond (2.335(4) Å), which is considerably greater than the sum of the covalent radii (2.13 Å), is also significantly longer than Sn-O distances reported for many tin complexes, including for example, dimethylchlorotin acetate (shortest Sn-O 2.165(6) Å)[9] and μ-bis (diphenylphosphinyl)ethane-bis(nitratotriphenyltin), Sn-O 2.220(5) Å[10]. It would appear that the tin-oxygen interaction in the present TPPO adduct is relatively weak and certainly the P-O distance shows only a slight lengthening upon coordination (from a mean value of 1.475 Å to 1.510(4) Å). The resulting P-O bond length is considerably shorter than the sum of the covalent radii (1.83 Å) and is indicative of the presence of substantial π-character. The coordination of the TPPO ligand is similar to that found in nitratotriphenyl(triphenylphosphine oxide)tin(IV)[11], where the Sn-O and P-O distances are 2.29(2) and 1.47(2) Å respectively. The Sn-O-P angle in this nitrato complex is 153(1)° and may be compared with that found in the present study (146.9(2)°).

## 3.4 Conclusions

The X-ray analyses confirm that tri-(3-thienyl) tin bromide has a discrete tetrahedral geometry and the triphenylphosphine oxide adduct has a trigonal bipyramidal structure with equatorial heteroaryl groups. The results obtained emphasise the utility of the Mössbauer technique in predicting the solid state structures of organotin compounds. It should be noted, however, that where the quadrupole splitting parameter or the commonly used Herber Ratio (isomer shift/quadrupole splitting) does not provide a definite assignment of the coordination about tin,[12,13] structural assignments should not be made without the support of additional data. Unfortunately, the air (moisture) instability of the 2-heteroaryltin derivatives has precluded X-ray crystallographic studies. An investigation of tri-(2-furyl)tin chloride would perhaps have been of most interest in view of the probable electron withdrawing properties of the 2-furyl and chlorine groups and the electron donating capabilities of oxygen in the formation of a coordinate bond.

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## Appendix

## Principles of $^{119m}$Sn Mössbauer Spectroscopy

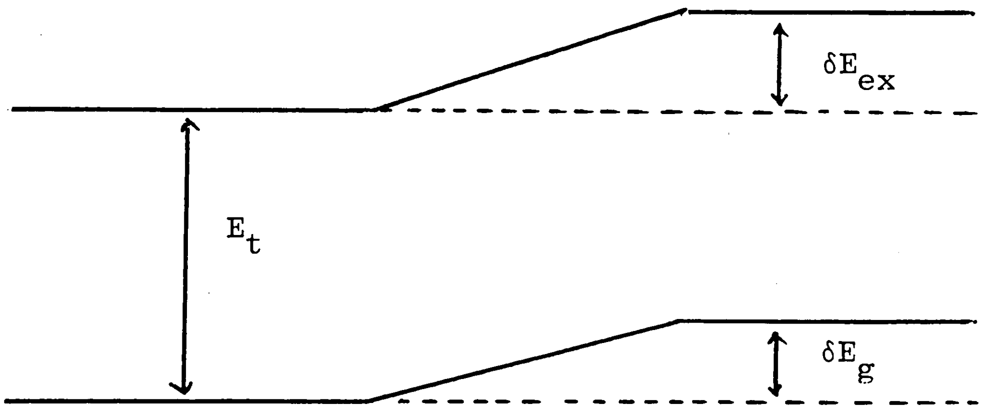
Resonance Fluorescence in atomic systems is well known and provides the basis for the established technique of fluorescence spectroscopy, widely employed in analytical chemistry. The essential point is that an atom in an excited electronic state eventually decays to the ground state with the emission of a photon. This can then be absorbed by another atom during electronic excitation and the subsequent de-excitation and re-emission of the photon in random directions gives rise to scattering or resonant fluorescence. The Mössbauer effect[1,2] forms the basis for high resolution NUCLEAR fluorescence spectroscopy. When many radioactive nuclei in excited states decay it would seem possible that the $\gamma$-rays omitted from this source might excite other stable nuclei of the same isotope in an absorber to provide nuclear resonant absorption and fluorescence.

Although the Mössbauer effect offers the highest energy resolution of any spectroscopic technique, two fundamental problems became apparent during early studies on this effect: Doppler Broadening and Nuclear Recoil. Thermal Doppler broadening greatly increases the natural line width for a transition and thereby reduces the intrinsic resolution. Nuclear recoil gives rise to a displacement of the emission and absorption lines resulting in little or no spectral overlap. Mössbauer's fundamental observation was that these destructive effects could be eliminated by considering the behaviour of the recoiling nucleus when it was no longer isolated, but fixed in a crystal lattice. With the emitting nucleus secured in a rigid matrix it was found that the recoil momentum could, under certain special conditions, effectively be transferred to the infinite mass of the matrix, providing that the recoil energy is less than the lowest quantised lattice vibrational energy, and thereby undergo emission without energy loss. Such recoilless emission is optimised for low energy $\gamma$-rays from nuclei strongly bound in a crystal lattice at low temperatures. Doppler broadening is a consequence of the random thermal velocities of the source and aborber nucleii. However, if the nucleus is isolated from the vibrational modes of the lattice during the emission and absorption process then Doppler broadening is eliminated.

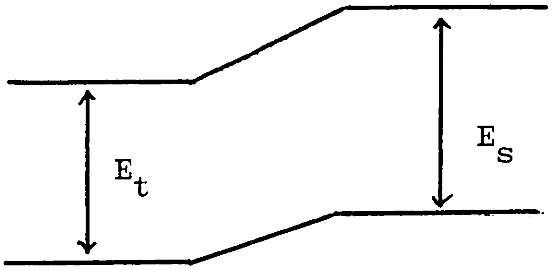
Applications of the Mössbauer effect make use of its extremely high energy resolution. The narrow line widths are often comparable with or less than the interaction energies (the so called Hyperfine Interactions) between the nuclei and their associated electrons. One important application of Mössbauer Spectroscopy is the study of the strength and nature of these interactions in different electronic, chemical and magnetic states of the atom. To simplify the interpretation of experimental data it is usual to study the Hyperfine Interactions in a series of absorbers each containing the stable Mössbauer Isotope, while using a single line source. The three main Hyperfine Interactions which can be observed by Mössbauer Spectroscopy are reflected in the Mössbauer parameters known as chemical isomer shifts, quadrupole splittings and magnetic splittings. In the application of $^{119m}$Sn Mössbauer spectroscopy in this study only the isomer shift and quadrupole splitting parameters are significant.

### The Isomer Shift ($\delta$)

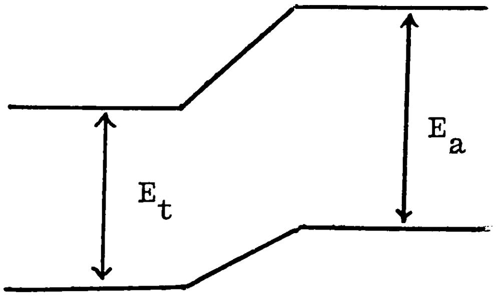
The nucleus, which has a finite volume, is surrounded and penetrated by electronic charge with which it interacts electrostatically. A change in 's' electron density, i.e. those electrons which possess a finite probability of being present at the nucleus, will give rise to a change in the Coulomb Interaction which produces a shift in the nuclear energy levels. The term isomer shift relates to the difference in electrostatic interaction resulting from the difference in the nuclear radii of the ground and isomeric excited states. Hence the spacing of the Nuclear energy levels depends on the 's' electron density at the nucleus. Changes in this density therefore give rise to shifts in the relative energy of the resonance line.



In the Mössbauer experiment the small change in energy between the ground state and the excited state ( $\delta$Eex - $\delta$Eg) for a standard source material and an absorber is measured.



Source (s)

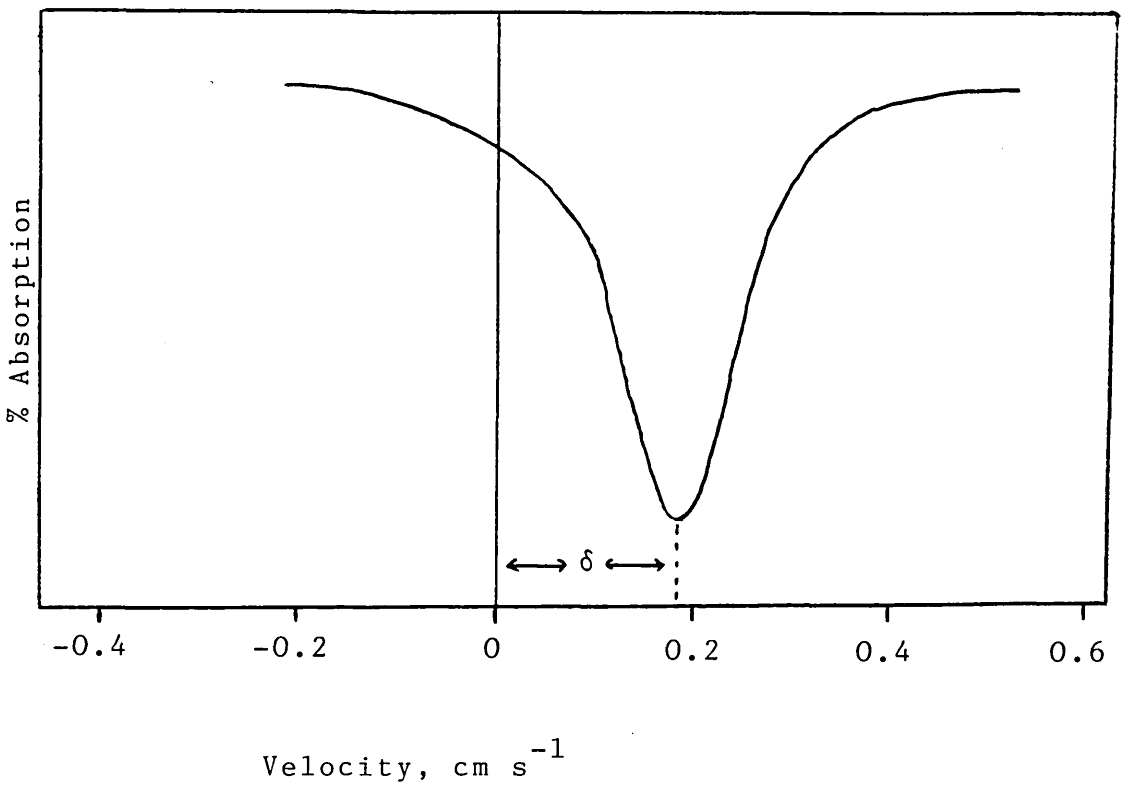


Absorber (a)

Thus Isomer Shift = $\delta = E_a - E_s$

For $^{119m}$Sn, an increase in 's' electron density at the absorber nucleus results in a positive isomer shift. Tin compounds having minimum 's' electron densities ($SnO_2$, $CaSnO_3$, $BaSnO_3$) are used as standard sources. All other tin absorbers then give zero or positive isomer shifts relative to the source.

An example of Isomer Shift (δ)

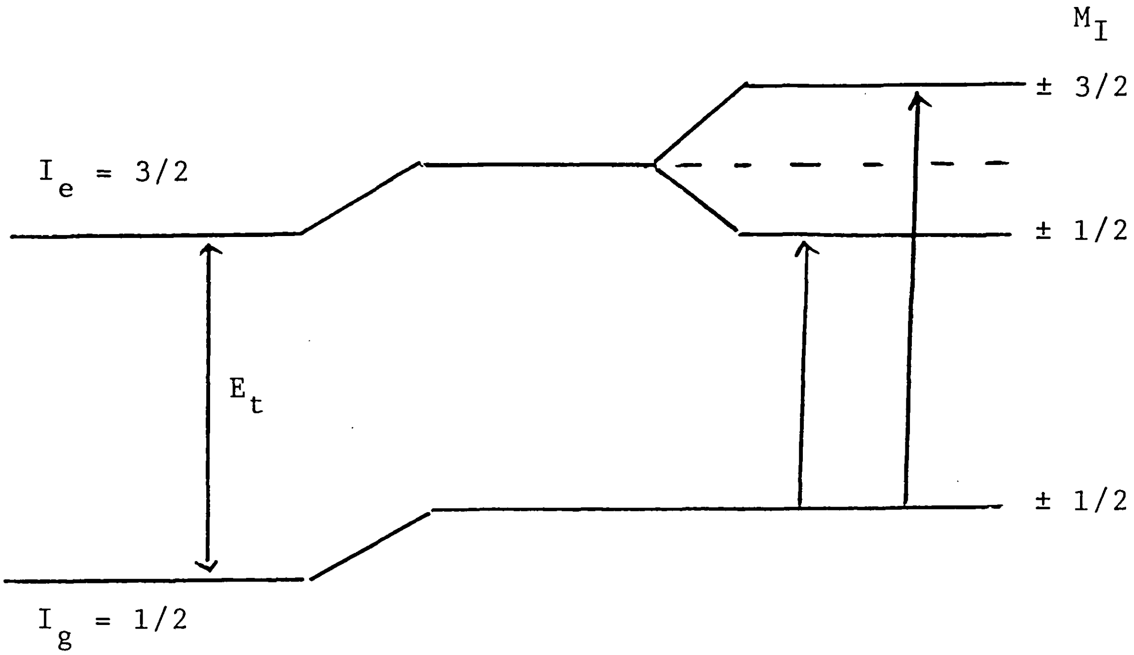


Mössbauer Spectroscopy therefore provides a means of monitoring the 's' electron density at the nucleus both directly and indirectly where changes in electron density are due to electrons in other types of orbital particupating in the chemical bond. The effective 's' electron density at the nucleus is dependent on the 'p', 'd' and 'f' electron disposition and provides a measure by which atomic oxidation states may be directly investigated. Tin in the neutral state has the electronic configuration: [Kr] $4d^{10}5s^{2}5p^{2}$. In the extreme case of completely ionic stannic compounds the valence configuration is $4d^{10}$ and for the tin II (stannous) compounds the ionic configuration is $4d^{10}5s^{2}$. As expected the stannous compounds exhibit the largest isomer shift values, the removal of the two 5p electrons reducing any shielding effect on the 5s electrons and thereby increasing 's' electron density at the tin nucleus. In the case of the ionic stannic compounds both the 5p and 5s electrons are removed and thus the loss of two 5s electrons markedly reduces the $^{119}Sn$ isomer shift. Covalent compounds have an intermediate number of 5s electrons depending on the nature of the hybridisation and on the partial ionic character of the bonds involved. In the series $SnI_4$, $SnBr_4$, $SnCl_4$ and $SnF_4$ the observed decrease in isomer shift corresponds to a decrease in the density of 5s electrons associated with the tin nucleus and represents an increase in the partial ionic character of the chemical bonds. Correspondingly, for the divalent tin compounds an increase in Isomer shift represents increased ionic character within the tin(II) bonds i.e. a tendency from $5s^2$ $5p^2$ (covalent) towards $5s^2$ (ionic), the 5p electrons screening the nucleus from the 5s electrons. Thus the isomer shift values also provide a quantitative assessment of the electron-withdrawing power of substituent electronegative groups. Furthermore the degree of $\pi$-bonding and back donation from metal atoms to ligands in coordination complexes can be investigated.

## The Quadrupole Interaction

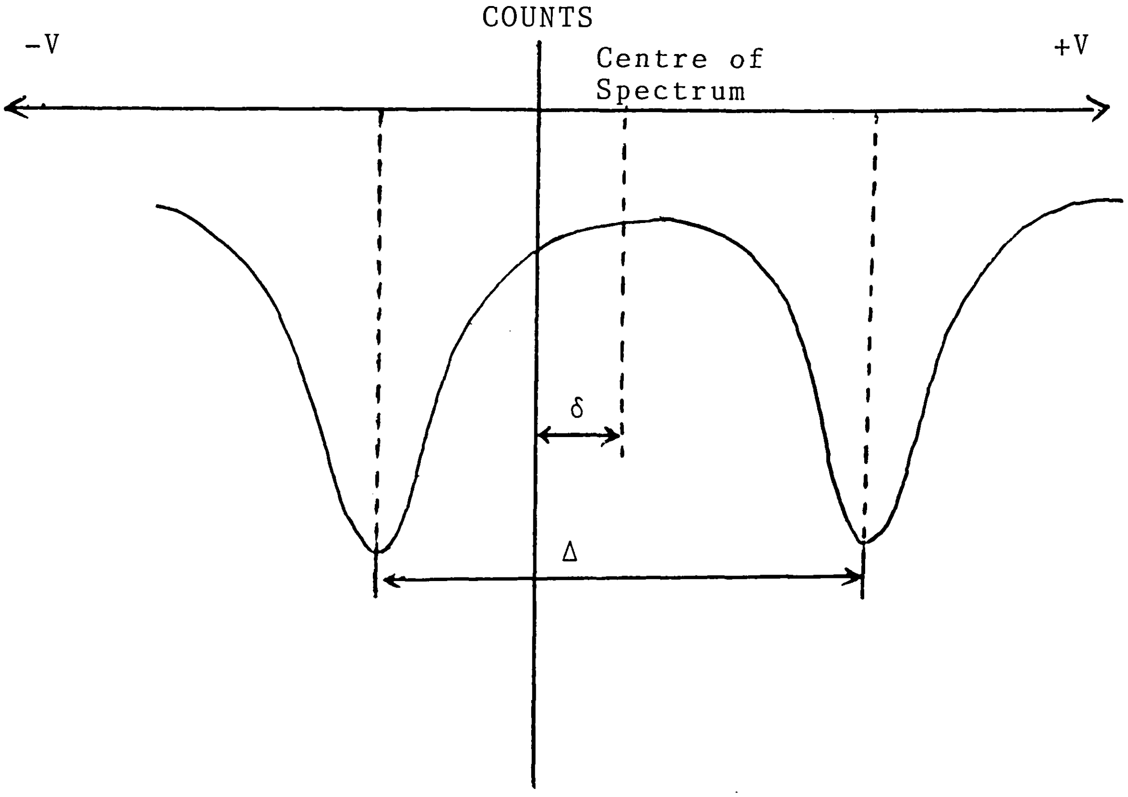
The principles employed in the derivation of the isomer shift assume the nucleus to be a sphere having uniform charge density, the Spin Angular Momentum, $(I) = 0$ or $\frac{1}{2}$, giving rise to zero quadrupole moment. However, for nuclei in which $I > \frac{1}{2}$, the charge density is no longer uniform and this gives rise to a Nuclear Quadrupole Moment, Q. The nuclear quadrupole moment may align itself with or across any local electric field gradient. When this occurs the degeneracy of the energy levels is partially removed. For tin, the ground state spin $I_g = \frac{1}{2}$ and the excited state spin $I_e = 3/2$. As nuclei with spin = 0 or $\frac{1}{2}$ are spherically symmetrical the $I_g = \frac{1}{2}$ level cannot exhibit a quadrupole interaction and therefore remains degenerate. However, the $I_e = 3/2$ level splits into two sub-levels $m_I = \pm \frac{1}{2}$, (FIG. A1). Thus two transitions are now possible.

FIG. A1



Under normal conditions both transitions occur with equal probability giving a characteristic two line spectrum of equal line intensity. In general there will be a combined Isomer Shift, $\delta$, and Quadrupole Splitting Interaction, $\Delta$, FIG. A2.

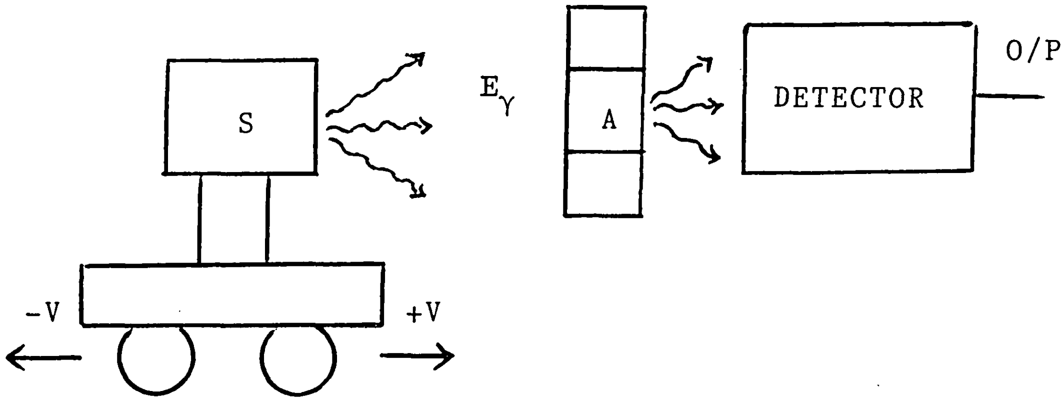
FIG.A2



The Mössbauer quadrupole splitting parameter, $\Delta$ , therefore provides information about the symmetry of the site occupied by the Mössbauer atom and the electric field gradient at the nucleus. The parameter is a very sensitive means of detecting small departures from ideal symmetry. The electric field gradient arises from non-spherical charge distribution around the nucleus and the distribution of point charges (ligands) will therefore affect the quadrupole splitting parameter very greatly. The electric field gradient has two sources; a valence contribution from the electrons present in unfilled atomic orbitals and a lattice contribution associated with the distant ionic charges of ligands. As previously mentioned 's' electron orbitals have spherical symmetry and as such do not contribute to the quadrupole interaction. It is the asymmetric charge distribution of valence 'p' electrons which produce large field gradients at the nucleus. Furthermore, when all three 5p orbitals are equally populated, then the px and py orbitals each produce field gradients of half the magnitude and opposite in sign to that of the $p_z$ orbital. Thus, the superposition of the three orbitals again forms a spherically symmetric charge distribution. Large values of $\Delta$ are therefore only observed in covalent tin compounds in which there is unequal population of the three 5p or four $sp^3$ orbitals. The long range field gradients produced by neighbouring ions are, in general, considerably smaller.

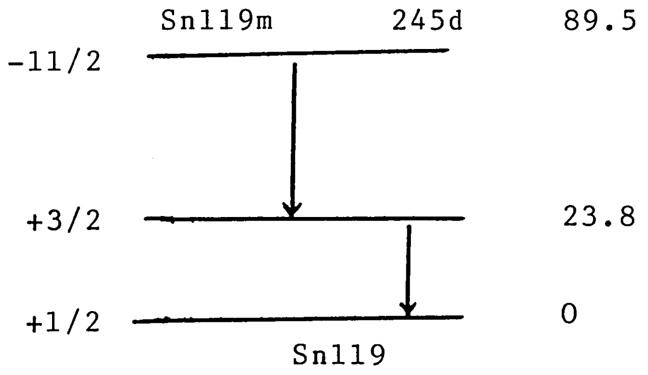
## EXPERIMENTAL METHOD

A transmission Mössbauer spectrum is a plot of the number of $\gamma$-ray photons transmitted by a sample, as a function of the instantaneous Doppler velocity of the source with respect to the absorber. The detector is used to observe the radiation which is transmitted through the absorber to the detector. Where resonance absorption occurs, an absorption peak will arise. In order to observe this resonance the source is mounted on a transducer which, at constant acceleration, moves towards and away from the stationary absorber, FIG. A3.



Thus a constant acceleration spectrometer sweeps through a selected velocity range, where each velocity corresponds to a particular corresponding Doppler energy value, and collects the Mössbauer spectrum in a multichannel analyser. In the multichannel analyser the spectrum is accumulated over 512 channels, each channel represents a particular $\gamma$-ray energy corresponding to a specific Doppler velocity. Once stored in the multichannel analyser, the spectrum is then available for computer processing.

The source employed for the investigation of organotin compounds was a 15mCi $^{119m}$Sn isotope in a $BaSnO_3$ matrix. The decay scheme for this isotope can be seen in figure A4.



The $\gamma$-ray decay of $^{119m}$Sn results in the emission of a 23.8 KeV $\gamma$-ray with a source line width close to the natural line width for this emission. This provides good resolution and facilitates the interpretation of complex spectra. Additionally, the recoilless fraction is sufficiently high to allow the source to be used at room temperature.

## Absorbers

Nearly all the samples analysed were reasonably pure solids or neat liquids at room temperature. The solids were packed into perspex discs and sealed. For the liquid samples, sealed discs were prepared and then drilled to allow the injection of the sample, the hole was then resealed. For some of the more unstable samples, considerable care was taken to prepare the discs in an inert atmosphere. Once prepared, the absorbers were cooled to 80K in a liquid nitrogen cryostat. As well as increasing the recoilless fraction of the absorber, the reduced temperature and inert atmosphere aided the characterisation of compounds whose instability had precluded their investigation by other techniques. The instrument was calibrated using the six-line magnetic spectrum obtained from a sample of enriched iron.

## Data Handling

A computer programme was used to interpret the raw Mössbauer data in terms of line position, line width and relative intensity of lines. As the constant acceleration spectrometer sweeps through the selected velocity range in cycles, the multichannel analyser stores two mirror-image spectra resulting from the forward and backward motion of the source relative to the absorber. The computer program first folds the data to give the best overlap of the mirror images.

This is achieved by scanning the folded data over an offset of ± 10 half channels and minimising the sum of the squares of the differences of the two spectra. The point where this minimum occurs defines the folding position in channels. Using the folded data, the peak positions, widths and relative intensities (in channels) are estimated manually. These estimates are then used as starting parameters for the non-linear least squares fitting program. This program is used to:

(i) calculate a set of theoretical Lorentzian absorption lines;

(ii) calculate a minimum in the differences between the sum of the squares of the actual spectrum and the theoretical one. This defines the $\chi^2$ (chi-squared) value which has the expression

$$\chi^2 = \sum_{i=0}^{i=256} (x_i^{\text{exp}} - x_i^{\text{theory}})^2$$

If the experimental and theoretically derived spectra are poorly matched, or background scatter is high, then $\chi^2$ will be large.

The positions of the absorption lines can then be used to calculate isomer shift and quadrupole splitting values for $^{119}$Sn Mössbauer doublets or provide directly the isomer shift values for Mössbauer singlets.

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1. The Chemistry of Organometallic Compounds, ten lectures, Dr N. A. Bell, Sheffield City Polytechnic, 1981.
2. Physical Techniques and Inorganic Chemistry, ten lectures, Dr B. E. Mann, University of Sheffield, 1981.
3. Introduction to Mossbauer Spectroscopy, ten lectures, Dr J. S. Brooks, Sheffield City Polytechnic, 1981.
4. The Royal Society of Chemistry Mossbauer Discussion Group Meetings:
   - i) Sheffield City Polytechnic, July 1981.
   - ii) University of Essex, July 1982.
5. The Fourth International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin and Lead, McGill University, Montreal, Quebec, Canada, August 1983.

*Journal of Organometallic Chemistry*, 251 (1983) 45–52
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# HETEROARYLTIN COMPOUNDS. THE CHEMISTRY AND $^{119}$Sn MÖSSBAUER SPECTROSCOPY OF SOME 3-THIENYLTIN HALIDES, AND A COMPARISON WITH 2-THIENYL AND 2-FURYL ANALOGUES

DAVID W. ALLEN, D. JANE DERBYSHIRE,
*Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield, S1 1WB (Great Britain)*

JOHN S. BROOKS,
*Department of Applied Physics, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB (Great Britain)*

and PETER J. SMITH
*International Tin Research Institute, Fraser Road, Perivale, Greenford, Middlesex, UB6 7AQ (Great Britain)*

(Received January 31st, 1983)

## Summary

The preparation of a range of (3-thienyl)tin halides, $(3\text{-}C_4H_3S)_nSnX_{4-n}$ ($n = 2$ or 3; X = Cl, Br or I), and some complexes with donor ligands, is described. Mössbauer spectroscopy indicates that the halides have unassociated, tetrahedral, structures. The related 2-thienyl- (and 2-furyl-) tin halides have also been prepared and characterised by Mössbauer spectroscopy, but are much less stable.

## Introduction

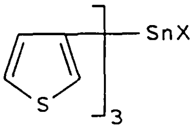
Apart from various symmetrical and unsymmetrical tetraorganostannanes [1], very little is known of the chemistry of tin compounds bearing a heteroaryl group directly linked to tin via a carbon atom of the heterocyclic ring. In view of the great variety of heterocyclic ring systems, and the established biological activity of organotin compounds of the types $R_3SnX$ [2], together with the recent interest in complexes of diorganotin compounds, $R_2SnX_2$, as possible antitumour agents [3], we have commenced an exploration of the preparation, structures and properties of heteroarylorganotin compounds of the above types. In this paper we describe the chemistry of some 3-thienyltin derivatives, together with a preliminary report of related 2-thienyl and 2-furyl systems. Prior to this study, as far as we are aware, the only reported examples of compounds of these types are di(2-thienyl)tin dichloride [4], (prepared by a redistribution reaction between tetra(2-thienyl)tin and stannic chloride and characterised by conversion to related tetraorganostannanes $R_2Sn(C_4H_3S\text{-}2)_2$) and di(2-thienyl)tin diiodide [5] (prepared by a direct synthesis

0022-328X/83/$03.00

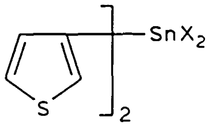
from metallic tin and 2-iodothiophen and characterised by replacement of the iodines by a series of chelating anionic ligands).

## Results and discussion

The tri(3-thienyl)tin halides (I, X = Cl, Br, I) were obtained by the redistribution reactions of tetra(3-thienyl)tin (3 mol) with the appropriate stannic halide (1 mol). Whereas the reactions with stannic chloride and bromide were conducted in the absence of a solvent at ~ 150°C and were complete in a relatively short time, (ca. 1–2 h), the reaction with stannic iodide proceded more slowly. At the prevailing temperature, sublimation of stannic iodide proved to be a problem, and hence the conversion was carried out under prolonged reflux in toluene solution. The resulting triorganotin halides were purified by recrystallisation and isolated as air-stable, analytically pure solids. Of the three halides, the iodide appeared to have the lowest thermal stability, there being some evidence of decomposition on recrystallisation.



(I)



(II)

The Mössbauer spectra of the solids (recorded at 80 K) all show quadrupole-split doublets without line broadening, with parameters similar to those of the related phenyltin halides (Table 1, Fig. 1). The magnitude of the quadrupole splitting (and of the Herber ratio $\Delta/\delta$ [6]) are indicative of four coordination 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 interactions between the thienyl sulphur of one ring system and the tin atom of another molecule. We are currently carrying out X-ray studies of the chloride and bromide of the above series in order to clarify this point. Comparison of the Mössbauer data for these compounds with that for the related phenyltin halides reveals that both the isomer shift and the quadrupole

TABLE 1

MÖSSBAUER DATA FOR TRI(3-THIENYL)TIN HALIDES AND RELATED COMPOUNDS

| | Isomer shift, [a] $\delta$ (mm/s $\pm$ 0.02) | Quadrupole splitting, $\Delta$ (mm/s $\pm$ 0.02) |
|---|---|---|
| $(3\text{-}C_4H_3S)_3SnCl$ | 1.21 | 2.29 |
| $(3\text{-}C_4H_3S)_3SnBr$ | 1.25 | 2.08 |
| $(3\text{-}C_4H_3S)_3SnI$ | 1.29 | 2.02 |
| $(3\text{-}C_4H_3S)_3SnCl \cdot Ph_3PO$ | 1.18 | 3.08 |
| $(3\text{-}C_4H_3S)_3SnBr \cdot Ph_3PO$ | 1.21 | 3.03 |
| $Ph_3SnCl$ | 1.37 | 2.45 [6] |
| $Ph_3SnBr$ | 1.37 | 2.46 |
| $Ph_3SnI$ | 1.41 | 2.05 [10] |

[a] Relative to $BaSnO_3$.

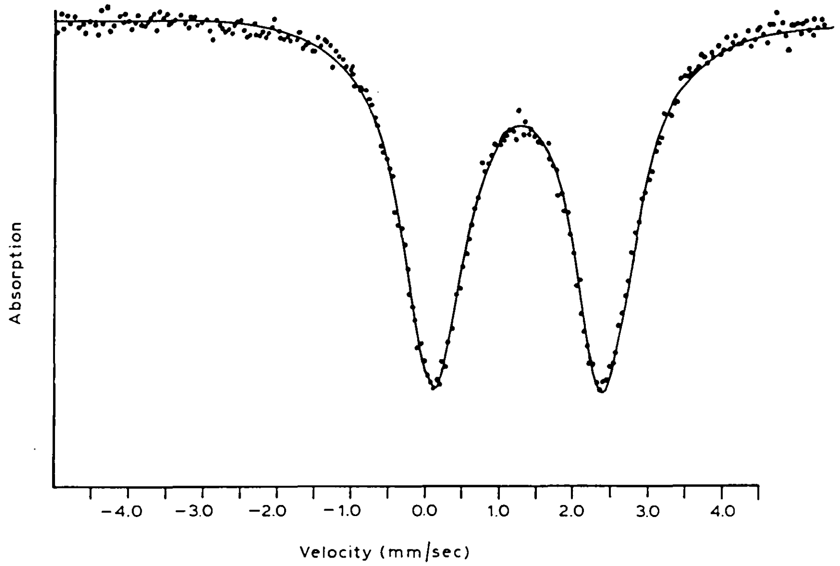


Fig. 1. Mössbauer spectrum of Tri(3-thienyl)tin chloride at 80 K.

splitting of the 3-thienyl derivatives are lower than those of the phenyl analogues. The reduction in isomer shift implies a reduction in *s*-electron density at tin, indicating that the 3-thienyl substituent is more electron-withdrawing than phenyl.

Treatment of the chloride (I, X = Cl) with an excess of *p*-tolylmagnesium bromide in ether gave the expected tri(3-thienyl)(*p*-tolyl)stannane. Both the chloride and bromide readily formed insoluble 1:1 complexes on treatment with equimolar amounts of triphenylphosphine oxide in toluene solution. Coordination of the phosphoryl oxygen is indicated by a significant reduction in the P=O infrared stretching frequency, compared with that of the free ligand, as observed for the related complex of triphenyltin chloride [7]. The Mössbauer parameters of the complexes (Table 1) are very similar to those reported for the triphenylphosphine oxide complexes of triphenyltin chloride and bromide, for which trigonal bipyramidal structures involving equatorial phenyl groups have been assumed on the basis of partial quadrupole splitting (p.q.s.) calculations [8,9].

The diorganotin dihalides (II, X = Cl or Br) have also been obtained by redistribution reactions of equimolar quantities of tetra(3-thienyl)tin with stannic halides. Both chloride and bromide were liquids which we were unable to crystallise. The related iodo derivative was obtained by direct synthesis from metallic tin and 3-iodothiophen, in the presence of pyridine hydrochloride as catalyst, according to the procedure reported by Gopinathan [5] for the synthesis of the related 2-thienyl analogue. After heating the reactants together at 150°C for several hours, the reaction mixture was distilled under reduced pressure to give a mixture of a mobile yellow oil, and a crystalline solid. A red solid, almost certainly stannic iodide, was also observed on the wall of the condenser. TLC of the distillate indicated that it consisted of two components, one of which was tetra(3-thienyl)tin and the other the diorganotin dihalide, the latter giving a characteristic blue colouration on spraying with catechol violet. The Mössbauer spectrum of this mixture showed an asymmetric

TABLE 2

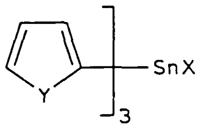
MÖSSBAUER DATA FOR DI(3-THIENYL)TIN DIHALIDES AND RELATED COMPOUNDS

| | Isomer shift, $\delta$ (mm/s $\pm$ 0.02) [a] | Quadrupole splitting, $\Delta$ (mm/s $\pm$ 0.02) |
|---|---|---|
| $(3\text{-}C_4H_3S)_2SnCl_2$ | 1.23 | 2.55 |
| $(3\text{-}C_4H_3S)_2SnBr_2$ | 1.30 | 2.30 |
| $(3\text{-}C_4H_3S)_2SnI_2$ | 1.29 | 2.01 |
| $(3\text{-}C_4H_3S)_2SnCl_2\cdot$bipy | 0.86 | 2.00 |
| $(3\text{-}C_4H_3S)_2SnBr_2\cdot$bipy | 1.22 | 3.26 |
| $Ph_2SnCl_2$ | 1.34 | 2.89 [10] |
| $Ph_2SnBr_2$ | 1.43 | 2.54 [12] |
| $Ph_2SnI_2$ | 1.51 | 2.38 [12] |

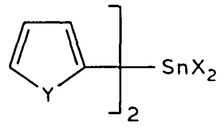
[a] Relative to $BaSnO_3$.

doublet, consistent with the presence of a mixture of di(3-thienyl)tin diiodide and tetra(3-thienyl)tin.

The Mössbauer spectra of the diorganotin dihalides (Table 2) reveal the expected quadrupole-split doublets, and the magnitude of the quadrupole-splitting is indicative of four coordinated tin, in unassociated, discrete, molecules. As for the related tri(3-thienyl)tin halides, the values of both the isomer shift and quadrupole splitting parameters are smaller than for those of the related diphenyltin dihalides, again consistent with the greater electron-withdrawing effect of the 3-thienyl group compared to phenyl. Both the dichloride and the dibromide were characterised by formation of 1:1 complexes with 2,2′-bipyridyl on treatment of the dihalide with an equimolar amount of 2,2′-bipyridyl in toluene solution. Mössbauer data for the complexes (Table 2) are consistent with a *cis*-octahedral structure for the dichloro complex and a distorted *trans*-octahedral structure for the dibromo complex, by analogy with Mössbauer data for related complexes [11]. As expected, treatment of the di(3-thienyl)tin dichloride with *p*-tolylmagnesium bromide in ether gave di(3-thienyl)di(*p*-tolyl)tin, as a stable solid.



(III)



(IV)

We have also made a study of the preparation and properties of related 2-furyl- and 2-thienyl organotin compounds (III, IV, Y = O or S, X = Cl, Br or I), and now present our initial findings. The triorganotin halides were all obtained by the redistribution reactions of tetra-(2-heteroaryl)stannanes with the appropriate stannic halide. Without exception, these compounds have been found to be unstable, readily decomposing on attempted recrystallisation, or even on standing at room temperature. Traces of moisture readily cause their decomposition to stannic oxide. We have, however, obtained the Mössbauer spectra of these compounds immediately following their formation, and the parameters are presented in Table 3. All the spectra consist

TABLE 3

MÖSSBAUER DATA FOR 2-FURYL- AND 2-THIENYL-TIN HALIDES

| | Isomer shift, $\delta$ (mm/s $\pm$ 0.02) [a] | Quadrupole splitting, $\Delta$ (mm/s $\pm$ 0.02) |
|---|---|---|
| *(i)* $R_3SnX$ | | |
| $(2\text{-}C_4H_3O)_3SnCl$ | 1.14 | 2.14 |
| $(2\text{-}C_4H_3O)_3SnBr$ | 1.17 | 2.19 |
| $(2\text{-}C_4H_3O)_3SnI$ | 1.23 | 1.84 |
| $(2\text{-}C_4H_3S)_3SnCl$ | 1.13 | 1.99 |
| $(2\text{-}C_4H_3S)_3SnBr$ | 1.18 | 1.99 |
| $(2\text{-}C_4H_3S)_3SnI$ | 1.20 | 1.77 |
| *(ii)* $R_2SnX_2$ | | |
| $(2\text{-}C_4H_3O)_2SnCl_2$ | 1.10 | 2.09 |
| $(2\text{-}C_4H_3O)_2SnBr_2$ | 1.17 | 1.80 |
| $(2\text{-}C_4H_3O)_2SnI_2$ | 1.34 | 1.42 |
| $(2\text{-}C_4H_3S)_2SnCl_2$ | 1.14 | 2.06 |
| $(2\text{-}C_4H_3S)_2SnBr_2$ | 1.21 | 1.96 |
| $(2\text{-}C_4H_3S)_2SnI_2$ | 1.26 | 1.84 |

[a] Relative to $BaSnO_3$.

of a quadrupole-split doublet, the magnitude of the splitting indicating that the tin atom is four coordinate, as for the above 3-thienyl derivatives. Again, there is no evidence of intermolecular association leading to an increase in coordination number at tin. The related diorganotin dihalides have also been obtained by redistribution reactions, and were found to be similarly unstable. Of the dihalides, di(2-thienyl)tin diiodide was also prepared by the direct synthesis from tin metal and 2-iodothiophen, as described by Gopinathan. In our hands, distillation of the reaction mixture under reduced pressure gave, (as in the case of the 3-thienyl derivative), a mixture of tetra(2-thienyl)tin and the dihalide. The formation of tetra(2-thienyl)tin in this reaction was not reported by Gopinathan [5], and it would seem that the di(heteroaryl)tin diiodides are unstable and disproportionate on distillation. Indeed, attempts to purify other di(2-heteroaryl)tin halides by distillation under reduced pressure have also met with little success, the Mössbauer spectra of the distillates being of poorer quality than those of the initial reaction mixtures. The Mössbauer spectra of the di(2-heteroaryl)tin dihalides exhibit the expected quadrupole-split doublets, the magnitude of the splitting again being consistent with a four coordinate, unassociated structure (Table 3).

A comparison of Mössbauer isomer shifts for related compounds in Tables 1–3 indicates that the electron-withdrawing properties of the organic groups attached to tin appear to increase in the order phenyl < 3-thienyl < 2-thienyl ⩽ 2-furyl. This trend is also apparent in the case of the tetra(heteroaryl)stannanes (Table 4). In an earlier publication [13], we have considered the factors responsible for the significant decrease in the isomer shifts of tetra(2-furyl)- and -(2-thienyl)-stannanes compared to tetraphenyltin and related substituted arylstannanes, and concluded that the dominant factor is the electron-withdrawing effect of the heteroatoms. There would seem to be little tendency for such "$\pi$-excessive" heteroaromatic ring systems to be

TABLE 4

MÖSSBAUER DATA FOR TETRAHETEROARYLSTANNANES

| $Ar_4Sn$ | Isomer shift, $\delta$ (mm/s $\pm$ 0.02) [a] |
|---|---|
| Ar = 2-Furyl | 1.06 |
| Ar = 2-Thienyl | 1.10 |
| Ar = 3-Thienyl | 1.16 |
| Ar = Phenyl | 1.26 |

[a] Relative to $BaSnO_3$.

involved in $p_\pi \rightarrow d_\pi$ interactions with the tin atom. A similar pattern is evident from studies of the reactivity of a wide range of compounds of the main Group V elements [14].

The instability of the 2-heteroarylorganotin halides is presumably due to the ease with which they undergo protodestannylation reactions, a reflection of the tendency of furan and thiophen to undergo electrophilic substitution in the 2-position with great ease [15]. The increased stability of the 3-thienyl derivatives is again consistent with this point of view.

Our studies of the chemistry of heteroarylorganotin compounds are continuing, and attempts to characterise the unstable 2-heteroarylorganotin halides by complex formation are currently in hand, and meeting with some success.

## Experimental

All of the reactions described were carried out under an inert atmosphere of nitrogen or argon. Tetra(2-furyl)tin, tetra(2-thienyl)tin and tetra(3-thienyl)tin were prepared as described previously [16]. $^{119}$Sn Mössbauer spectra were obtained using a constant acceleration spectrometer. A 15 mCi $Ba^{119}SnO_3$ source was used at room temperature, and the samples were sealed in perspex discs and cooled to 80 K using a continuous flow nitrogen cryostat and helium exchange gas. The Mössbauer hyperfine parameters were obtained from computer least-squares fits to the spectra, using Lorentzian line shapes. $^1$H NMR spectra were recorded at 80 MHz using a Brüker WP80 SY FT spectrometer, using TMS as internal standard.

Compounds were prepared as follows:

*Tri(3-thienyl)tin chloride.* Tetra(3-thienyl)tin (1.0 g, $2.2 \times 10^{-3}$ mol) and stannic chloride (0.08 cm$^3$, $7.81 \times 10^{-4}$ mol) were heated together with stirring at an oil bath temperature of 120°C for 1 h. The product crystallised on cooling, and was recrystallised from hexane-toluene. m.p. 103–104.5°C. Anal. Found: C, 35.75; H, 2.15; S, 23.95. $C_{12}H_9ClS_3Sn$ calcd.: C, 35.70; H, 2.25; S, 23.85%.

*Tri(3-thienyl)tin bromide.* Tetra(3-thienyl)tin (0.75 g, $1.66 \times 10^{-3}$ mol) and stannic bromide (0.24 g, $5.48 \times 10^{-4}$ mol) were heated together with stirring at an oil bath temperature of 170°C for 1 h. On cooling, the crude product was recrystallised from hexane-toluene. m.p. 115°C. Anal. Found: C, 32.30; H, 2.15; S, 21.15. $C_{12}H_9BrS_3Sn$ calcd.: C, 32.15; H, 2.05; S, 21.45%.

*Tri(3-thienyl)tin iodide.* Tetra(3-thienyl)tin (1.0 g, $2.2 \times 10^{-3}$ mol) and stannic iodide (0.46 g, $7.34 \times 10^{-4}$ mol) were heated together in toluene (7.5 cm$^3$) under reflux for 3 days. The colour of the solution gradually changed from orange to yellow. TLC indicated that some unreacted tetra(3-thienyl)tin was still present. On cooling, crystals were deposited, which were filtered off and extracted with hot chloroform. Evaporation of the chloroform extracts gave a solid which was recrystallised from hexane-toluene. m.p. 127–128°C. Anal. Found: C, 29.35; H, 1.80; S, 19.90; I, 25.75. $C_{12}H_9IS_3Sn$ calcd.: C, 29.10; H, 1.85; S, 19.45; I, 25.65%.

*Triphenylphosphine oxide complexes of tri(3-thienyl)tin halides.* A solution of the tri(3-thienyl)tin halide in toluene was treated in the cold with stirring with an equimolar amount of triphenylphosphine oxide, also dissolved in toluene. The following complexes crystallised from the solutions:

(a) Tri(3-thienyl)tin chloride · $Ph_3PO$, m.p. 142–144°C. Anal. Found: C, 53.00; H, 3.60; Cl, 5.00. $C_{30}H_{24}ClOPS_3Sn$ calcd.: C, 52.85; H, 3.55; Cl, 5.20%. Infra-red (Nujol mull): 1145 and 1122 $cm^{-1}$ (coordinated P=O),

(b) Tri(3-thienyl)tin bromide · $Ph_3PO$, m.p. 137–140°C. Anal. Found: C, 49.65; H, 3.35; S, 13.40. $C_{30}H_{24}BrOPS_3Sn$ calcd.: C, 49.60; H, 3.35; S, 13.25%. IR (Nujol mull): 1140 and 1119 $cm^{-1}$ (coordinated P=O).

*Tri(3-thienyl)(p-tolyl)stannane.* Tri(3-thienyl)tin chloride (0.68 g, $1.69 \times 10^{-3}$ mol) was dissolved in dry THF (5 $cm^3$) and treated with a solution of the Grignard reagent prepared from *p*-bromotoluene (0.56 g, $3.39 \times 10^{-3}$ mol) and magnesium (0.1 g, $4.12 \times 10^{-3}$ mol) in THF (8 $cm^3$). The resulting reaction mixture was stirred overnight, and then hydrolysed with aqueous ammonium chloride. The organic layer was separated, dried, and evaporated. The residue was recrystallised from isopropanol to give crystals, m.p. 119–121°C. Anal. Found: C, 49.50; H, 3.45; S, 20.95. $C_{19}H_{16}S_3Sn$ calcd.: C, 49.7; H, 3.50; S, 20.95%. $^1H$ NMR ($CDCl_3$): $\delta$ 7.1–7.9, (m, 13 ArH); 2.35 (s, 3H) ppm.

*Di(3-thienyl)tin dichloride-2,2′-bipyridyl complex.* Tetra(3-thienyl)tin (1.0 g, $2.22 \times 10^{-3}$ mol) and stannic chloride (0.25 $cm^3$, $2.22 \times 10^{-3}$ mol) were heated together with stirring at an oil bath temperature of 85°C for 1.5 h. The resulting liquid was dissolved in a mixture of chloroform and toluene (1/1 v/v), to which was added with stirring a similar solution of 2,2′-bipyridyl (0.69 g). The resulting solution rapidly deposited a white solid, which was filtered, washed with toluene and dried. m.p. 242°C. Anal. Found: C, 42.60; H, 2.80; N, 5.25. $C_{18}H_{14}Cl_2N_2S_2Sn$ calcd.: C, 42.20; H, 2.75; N, 5.45%.

*Di(3-thienyl)tin dibromide-2,2′-bipyridyl complex.* Tetra(3-thienyl)tin (1.0 g, $2.22 \times 10^{-3}$ mol) and stannic bromide (0.97 g, $2.21 \times 10^{-3}$ mol) were heated together with stirring at an oil bath temperature of 90°C for 2 h. The resulting liquid was dissolved in toluene and treated with a toluene solution of 2,2′-bipyridyl (1.38 g) to give the complex, m.p. 253°C (decomp.). Anal. Found: C, 35.65; H, 2.30; N, 4.45. $C_{18}H_{14}Br_2N_2S_2Sn$ calcd.: C, 35.95; H, 2.35; N, 4.65%.

*Di(3-thienyl)tin diiodide.* A mixture of 3-iodothiophen, (10 g, $4.76 \times 10^{-2}$ mol), alkali-washed, powdered tin (2.82 g, $2.38 \times 10^{-2}$ mol) and pyridine hydrochloride (0.06 g) was heated together under nitrogen with stirring overnight at an oil bath temperature of 150°C. The resulting deep yellow liquid was distilled under reduced pressure to give a fraction, b.p. 200–220°C at 0.05 mmHg, which crystallised on cooling. TLC analysis indicated the presence of both tetra(3-thienyl)tin and a diorganotin dihalide. The Mössbauer spectrum of the mixture was also indicative of the presence of tetra(3-thienyl)tin, and the parameters for di(3-thienyl)tin diiodide were obtained from computer fits to the combined data.

*Di(3-thienyl)(di-p-tolyl)stannane.* Di(3-thienyl)tin dichloride (from the reaction of tetra(3-thienyl)tin (1.0 g, $2.22 \times 10^{-3}$ mol) and stannic chloride (0.25 cm$^3$, $2.17 \times 10^{-3}$ mol)), dissolved in THF (8 cm$^3$) was treated with the Grignard reagent derived from *p*-bromotoluene (1.48 g, $8.65 \times 10^{-3}$ mol) and magnesium (0.25 g, $1.03 \times 10^{-2}$ mol) in THF (10 cm$^3$), and the resulting mixture stirred overnight. Treatment of the reaction mixture with aqueous ammonium chloride solution gave a white solid, which was dissolved by the addition of chloroform. Separation of the organic layer, followed by drying over anhydrous magnesium sulphate, and evaporation gave the stannane, m.p. 148–150°C, ex. isopropanol. Anal.: C, 56.3; H, 4.35; S, 13.85. $C_{22}H_{20}S_2Sn$ calcd.: C, 56.55; H, 4.30; S, 13.70%. $^1$H NMR ($CDCl_3$): $\delta$ 7.1–7.9, (m, 14 Ar H); 2.35, (s, 6H) ppm.

*Preparation of 2-thienyl- and 2-furyl-tin halides.* These were prepared by the redistribution reactions between the tetra(2-heteroaryl)stannane and the appropriate stannic halide, under conditions similar to those used as described above for the preparation of the (3-thienyl)tin halides. Di(2-thienyl)tin diiodide was also prepared as described by Gopinathan [5]. Immediately following their preparation, the compounds were sealed in perspex discs, and the Mössbauer spectra recorded at 80 K. Attempts to purify these compounds by recrystallisation were unsuccessful.

## Acknowledgements

The International Tin Research Council, London, is thanked for permission to publish this paper. D. Jane Derbyshire thanks SERC and the International Tin Research Institute for a CASE studentship.

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

**David W. Allen * and D. Jane Derbyshire**
*Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB*
**John S. Brooks**
*Department of Applied Physics, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB*
**Stephen J. Blunden and Peter J. Smith**
*International Tin Research Institute, Fraser Road, Perivale, Greenford, Middlesex, UB6 7AQ*

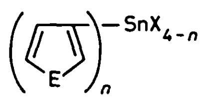
A series of 3-furyltin halides of the types $SnR_nX_{4-n}$ (R = 3-furyl; $n$ = 2 or 3; X = Cl or Br) have been prepared and characterised by chemical and spectroscopic techniques. Mössbauer data for triphenylphosphine oxide adducts of the tris(3-furyl)tin halides are consistent with five-co-ordinate 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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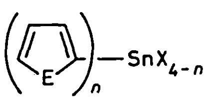

(2)

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-

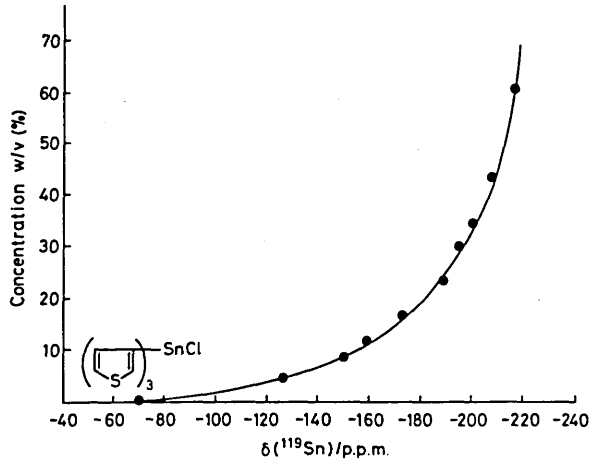

Figure 1. Concentration dependence of $^{119}$Sn n.m.r. chemical shift of the Sn(3-$C_4H_3S$)$_3$Cl·$Ph_3PO$ adduct in $CDCl_3$, at 33 °C

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 Sn(3-$C_4H_3S$)$_3$Cl·$Ph_3PO$ 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 $SnMe_{4-n}$(2-$C_4H_3O$)$_n$ 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 $SnEt_{4-n}Z_n$ ($n$ = 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 $d_\pi$ 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 $SnPh_4$ (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 Sn(3-$C_4H_3S$)$_4$ compared with Sn(3-$C_4H_3O$)$_4$ 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 $SnMe_3CF_3$ which is reported [18] to form a 1 : 1 complex with P($NMe_2$)$_3$. In addition, it is interesting to note that the $^{119}$Sn n.m.r. chemical shift of Sn[$C_6H_4$($CF_3$)-*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 $SnMe_4$ in similar solvents.[20] We find that there is a low frequency shift of 16 p.p.m. for Sn(2-$C_4H_3O$)$_4$ 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 Sn(2-$C_4H_3S$)$_4$ and, to a lesser extent, for Sn(3-$C_4H_3O$)$_4$ (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 $Ph_3PO$ to a solution of Sn(2-$C_4H_3O$)$_4$ in deuteriochloroform causes no shift in the $^{119}$Sn signal. However, when Sn(2-$C_4H_3O$)$_4$ and $Ph_3PO$ are melted together, the Mössbauer

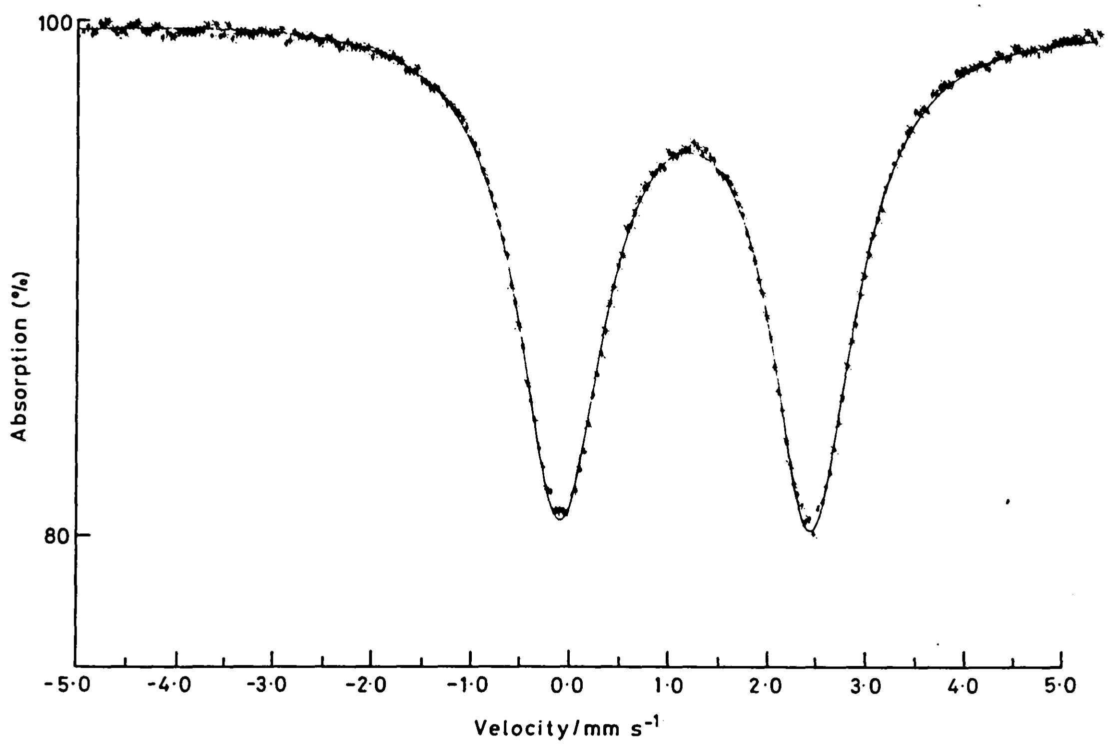

**Figure 2.** $^{119m}$Sn Mössbauer spectrum of $Sn(3\text{-}C_4H_3O)_2Cl_2$ at 80 K

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 $\pm 0.5$ p.p.m.

All the reactions described were carried out under an inert atmosphere of either nitrogen or argon. The compounds $Sn(3\text{-}C_4H_3O)_4$, $Sn(2\text{-}C_4H_3O)_4$, $Sn(2\text{-}C_4H_3S)_4$, and $Sn(3\text{-}C_4H_3S)_4$ 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*) $Sn(3\text{-}C_4H_3O)_3Cl{\cdot}Ph_3PO$ (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*) $Sn(3\text{-}C_4H_3O)_3Br{\cdot}Ph_3PO$ (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, $1.29 \times 10^{-3}$ mol) and $SnBr_4$ (0.56 g, $1.28 \times 10^{-3}$ 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, $2.56 \times 10^{-3}$ 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, $2.22 \times 10^{-3}$ mol) and $SnCl_4$ (0.25 cm$^3$, $2.17 \times 10^{-3}$ 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, $4.35 \times 10^{-3}$ 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, $1.29 \times 10^{-3}$ mol) and $SnBr_4$ (0.56 g, $1.28 \times 10^{-3}$ 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, $2.56 \times 10^{-3}$ 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, $1.29 \times 10^{-3}$ mol) and $SnBr_4$ (0.19 g, $4.33 \times 10^{-4}$ 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, $8.32 \times 10^{-4}$ 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 cm$^3$, $1.11 \times 10^{-1}$ mol) was added dropwise to benzo-[*b*]thiophen (17 g, $1.27 \times 10^{-1}$ mol) in dry diethyl ether (50 cm$^3$) with ice cooling. The reaction mixture was stirred at room temperature for 2 h. $SnCl_4$ (3.0 cm$^3$, $2.60 \times 10^{-2}$ 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 cm$^3$, $8.88 \times 10^{-2}$ mol) was added dropwise to benzo-[*b*]furan (12 g, $1.02 \times 10^{-1}$ mol) in diethyl ether (50 cm$^3$) with cooling (ice-salt) and stirred for 3 h. $SnCl_4$ (2.4 cm$^3$, $2.08 \times 10^{-2}$ 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%).

## Acknowledgements

The International Tin Research Council (London) is thanked for permission to publish this paper. D. J. D. thanks the S.E.R.C. and the International Tin Research Institute for a CASE studentship.

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*Received* 7*th November* 1983; *Paper* 3/1985

*Journal of Organometallic Chemistry*, 260 (1984) 263–270
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# CRYSTAL AND MOLECULAR STRUCTURE OF THE TRIPHENYLPHOSPHINE OXIDE ADDUCT OF TRI-3-THIENYLTIN BROMIDE, $Ph_3PO \cdot SnBr(C_4H_3S)_3$

DAVID W. ALLEN, D. JANE DERBYSHIRE, IAN W. NOWELL,
*Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB (Great Britain)*

and JOHN S. BROOKS
*Department of Applied Physics, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB (Great Britain)*

(Received September 15th, 1983)

## Summary

The solid state structure of the triphenylphosphine oxide (TPPO) adduct of tri-3-thienyltin bromide has been investigated by both single crystal X-ray analysis and Mössbauer spectroscopy. The crystal structure consists of discrete molecules and there is no evidence of any intermolecular tin–sulphur interactions. Each tin atom is found to be in a five-coordinate trigonal bipyramidal environment in which the three thienyl groups occupy equatorial positions. The metal atom is displaced by 0.182 Å out of the equatorial plane and towards the axial bromine. Two of the thienyl ligands exhibit rotational disorder and the lack of disorder in the remaining heteroaryl ligand is attributed to the close proximity of this group to a phenyl ligand. The Mössbauer parameters are also in accord with five-coordination for tin and are indicative of the aryl groups being equatorial.

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## Introduction

As part of our study of heteroaryltin(IV) compounds, we have investigated the solid state structure of a number of triorganotin halides. In order to substantiate Mössbauer data [1] an X-ray analysis of tri-3-thienyltin bromide was attempted. A preliminary study shows the molecule to be extensively disordered, with rotational disorder about the Sn–Br bond and also about each of the three Sn–C (thienyl) bonds. While it has not proven possible to gain detailed structural data, it has been established that the tin atom occupies a tetrahedral environment and that no intermolecular tin–sulphur interactions are present; a result in accord with the Mössbauer data. More recently we have prepared the triphenylphosphine oxide (TPPO) adduct of tri-3-thienyltin bromide and herein we present the X-ray analysis of this compound.

0022-328X/84/$03.00

## Experimental

Tri-3-thienyltin bromide and its TPPO adduct were prepared as previously described [1].

*Mössbauer data.* $^{119}$Sn Mössbauer spectra were obtained using a constant acceleration spectrometer. A 15mCi Ba$^{119}$SnO$_3$ source was used at room temperature, the samples were sealed in perspex discs and cooled to 80 K using a continuous flow nitrogen cryostat with helium exchange gas. The Mössbauer isomer shift and quadrupole splitting parameters were obtained from computer least squares fits to the spectra using Lorentzian line shapes.

*$^{119}$SnNMR.* $^{119}$Sn NMR spectra were recorded on a Jeol FX60Q instrument in 10 mm tubes at 22.24 MHz. The field frequency lock was to external D$_2$O.

*Crystal data.* $C_{30}H_{24}BrOPS_3Sn$, $M_r = 726.7$, triclinic, $P\bar{1}$, $a$ 14.700(10), $b$ 11.002(8), $c$ 9.805(7) Å, $\alpha$ 104.05(6), $\beta$ 95.04(5), $\gamma$ 101.71(5)°, $U$ 1490.5 Å$^3$, $Z = 2$, $D_c$ 1.62 Mg m$^{-3}$, $D_m$ 1.58 Mg m$^{-3}$, $\mu$(Mo-$K_\alpha$) 2.36 mm$^{-1}$, $F(000) = 720$.

### *Data collection and reduction*

Intensities were measured for a crystal, approximate dimensions 0.10 × 0.18 × 0.38 mm, mounted on a glass fibre with the $c$-axis coincident with the $\omega$-axis of a Stöe Stadi-2 two circle diffractometer. Monochromatic Mo-$K_\alpha$ radiation was used and the background-$\omega$ scan-background technique employed to give 4989 independent reflections, of which 4375 had $I \geqslant 3\sigma(I)$ and were used for subsequent analysis. Corrections were made for Lorentz and polarisation effects, but no correction was applied for absorption.

### *Structure determination and refinement*

Preliminary photographs showed the crystal to be triclinic and subsequent analysis confirmed the space group to be $P\bar{1}$. The approximate positions of the tin and bromine atoms were calculated from a three-dimensional Patterson synthesis and the remaining atoms were located from successive difference Fourier maps. While one of the 3-thienyl groups is ordered, the other two contain rotational disorder such that two thienyl groups (having approximately 50% occupancy) are related to each other by a pseudo two-fold axis about the Sn–C($n$1) ($n$ = 4,6) bonds. Each of the disordered 3-thienyl entities were given ideal geometries and included in the least squares refinement with common isotropic temperature factors applied to atoms related by the pseudo symmetry. The population parameters applied to each pair of thienyl units were refined, the final values corresponding to occupancies of 55 and 45% for the C($n$1), C($n$2A), S($n$3A), C($n$4A), C($n$5A) and C($n$1), C($n$2B), S($n$3B), C($n$4B), C($n$5B) moieties respectively. Hydrogen atoms were located for the three phenyl and ordered 3-thienyl groups, but given ideal geometry (C–H 1.08 Å). Common isotropic temperature factors were applied to the phenyl hydrogens and also to the thienyl hydrogens, which refined to final values of $U$ 0.088(9), 0.081(13) Å$^2$ respectively. Scattering factors were calculated using an analytical approximation [2] and the weighting scheme $w = 0.956/[\sigma^2(F_o) + 0.006(F_o)^2]$. All ordered, non-hydrogen, atoms were given anisotropic temperature factors and refinement converged at $R = 0.055$, $R' = 0.067$. Final position parameters are given in Table 1, bond

TABLE 1

FINAL POSITIONAL PARAMETERS ($\times 10^5$ for Sn and $\times 10^4$ for other atoms) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

| Atom | x | y | z |
|---|---|---|---|
| Sn | 27036(3) | 44611(4) | 20342(4) |
| Br | 3314(1) | 2338(1) | 1139(1) |
| P | 2349(1) | 7775(1) | 2983(1) |
| O | 2174(3) | 6341(3) | 2805(4) |
| C(11) | 2381(4) | 8601(5) | 4818(6) |
| C(12) | 2425(4) | 7924(6) | 5828(6) |
| C(13) | 2406(5) | 8531(8) | 7230(7) |
| C(14) | 2366(5) | 9791(8) | 7622(8) |
| C(15) | 2327(6) | 10454(7) | 6650(10) |
| C(16) | 2343(5) | 9905(6) | 5216(8) |
| C(21) | 3422(4) | 8402(5) | 2371(6) |
| C(22) | 4122(4) | 9421(6) | 3242(7) |
| C(23) | 4936(5) | 9825(7) | 2716(8) |
| C(24) | 5075(5) | 9242(8) | 1351(8) |
| C(25) | 4379(5) | 8257(7) | 506(7) |
| C(26) | 3551(4) | 7834(6) | 1018(7) |
| C(31) | 1381(4) | 8139(5) | 2018(6) |
| C(32) | 1445(5) | 8587(7) | 825(7) |
| C(33) | 625(7) | 8715(9) | 51(9) |
| C(34) | −232(6) | 8372(8) | 459(9) |
| C(35) | −277(5) | 8012(7) | 1692(10) |
| C(36) | 520(4) | 7873(7) | 2476(8) |
| C(41) | 1640 | 3608 | 3070 |
| C(42A) | 1060 | 4292 | 3766 |
| S(43A) | 169 | 3246 | 4207 |
| C(44A) | 699 | 1990 | 3796 |
| C(45A) | 1480 | 2305 | 3193 |
| C(42B) | 1698 | 2556 | 3556 |
| S(43B) | 615 | 1927 | 3955 |
| C(44B) | 247 | 3309 | 4017 |
| C(45B) | 868 | 4145 | 3526 |
| C(51) | 3997(4) | 5578(5) | 3262(6) |
| C(52) | 4771(5) | 6023(8) | 2722(9) |
| S(53) | 5666(2) | 6941(2) | 3996(4) |
| C(54) | 5059(6) | 6778(7) | 5251(9) |
| C(55) | 4157(5) | 5999(6) | 4764(7) |
| C(61) | 2297 | 4590 | −50 |
| C(62A) | 2762 | 4177 | −1156 |
| S(63A) | 2293 | 4550 | −2633 |
| C(64A) | 1396 | 5047 | −1843 |
| C(65A) | 1488 | 5055 | −454 |
| C(62B) | 1760 | 5419 | −292 |
| S(63B) | 1407 | 5096 | −2088 |
| C(64B) | 2437 | 4658 | −2366 |
| C(65B) | 2769 | 4234 | −1252 |
| H(12) | 2447 | 6920 | 5508 |
| H(13) | 2451 | 8018 | 8034 |
| H(14) | 2326 | 10259 | 8712 |
| H(15) | 2322 | 11463 | 6985 |
| H(16) | 2305 | 10444 | 4435 |
| H(22) | 4026 | 9873 | 4310 |
| H(23) | 5471 | 10628 | 3374 |

TABLE 1 (continued)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(24) | 5732 | 9540 | 977 |
| H(25) | 4465 | 7824 | −574 |
| H(26) | 3008 | 7044 | 356 |
| H(32) | 2117 | 8809 | 463 |
| H(33) | 676 | 9069 | −881 |
| H(34) | −851 | 8468 | −146 |
| H(35) | −952 | 7812 | 2052 |
| H(36) | 465 | 7534 | 3418 |
| H(52) | 4833 | 5794 | 1604 |
| H(54) | 5317 | 7248 | 6359 |
| H(55) | 3656 | 5736 | 5444 |

[a] Two of the three 3-thienyl groups are disordered. The first is comprised of C(41), C(42A), S(43A), C(44A), C(45A) and C(41), C(42B), S(43B), C(44B), C(45B) rings and the second of C(61), C(62A), S(63A), C(64A), C(65A) and C(61), C(62B), S(63B), C(64B), C(65B).

distances and angles in Table 2. The labelling scheme adopted is shown in Fig. 1. Lists of structure factors, thermal parameters and mean planes data are available on request from the authors (IWN).

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS FOR ORDERED ATOMS IN PARENTHESES

*Distances* (Å)

| | | | |
|---|---|---|---|
| Sn–Br | 2.651(1) | P–O | 1.510(4) |
| Sn–O | 2.335(4) | P–C(11) | 1.799(5) |
| Sn–C(41) | 2.121 | P–C(21) | 1.803(6) |
| Sn–C(51) | 2.122(5) | P–C(31) | 1.805(6) |
| Sn–C(61) | 2.125 | | |
| C(41)–C(42A) | 1.369 | C(41)–C(42B) | 1.369 |
| C(42A)–S(43A) | 1.720 | C(42B)–S(43B) | 1.720 |
| S(43A)–C(44A) | 1.703 | S(43B)–C(44B) | 1.704 |
| C(44A)–C(45A) | 1.359 | C(44B)–C(45B) | 1.365 |
| C(45A)–C(41) | 1.441 | C(45B)–C(41) | 1.439 |
| C(51)–C(52) | 1.349(10) | | |
| C(52)–S(53) | 1.694(7) | | |
| S(53)–C(54) | 1.606(10) | | |
| C(54)–C(55) | 1.396(10) | | |
| C(55)–C(51) | 1.416(8) | | |
| C(61)–C(62A) | 1.366 | C(61)–C(62B) | 1.369 |
| C(62A)–S(63A) | 1.723 | C(62B)–S(63B) | 1.719 |
| S(63A)–C(64A) | 1.704 | S(63B)–C(64B) | 1.704 |
| C(64A)–C(65A) | 1.355 | C(64B)–C(65B) | 1.377 |
| C(65A)–C(61) | 1.446 | C(65B)–C(61) | 1.433 |

TABLE 2 (continued)

| | *n* = 1 | *n* = 2 | *n* = 3 |
|---|---|---|---|
| C(*n*1)–C(*n*2) | 1.381(9) | 1.399(7) | 1.379(10) |
| C(*n*2)–C(*n*3) | 1.381(9) | 1.379(10) | 1.417(12) |
| C(*n*3)–C(*n*4) | 1.360(12) | 1.388(11) | 1.362(13) |
| C(*n*4)–C(*n*5) | 1.338(13) | 1.369(9) | 1.363(14) |
| C(*n*5)–C(*n*6) | 1.393(11) | 1.393(10) | 1.400(11) |
| C(*n*6)–C(*n*1) | 1.407(9) | 1.370(8) | 1.379(9) |

*Angles* (°)

| | | | |
|---|---|---|---|
| Br–Sn–O | 179.4(1) | C(51)–Sn–C(61) | 121.5(2) |
| Br–Sn–C(41) | 95.1 | P–O–Sn | 146.9(2) |
| Br–Sn–C(51) | 95.6(2) | O–P–C(11) | 110.0(3) |
| Br–Sn–C(61) | 94.0 | O–P–C(21) | 112.4(2) |
| O–Sn–C(41) | 85.5 | O–P–C(31) | 109.8(2) |
| O–Sn–C(51) | 84.3(2) | C(11)–P–C(21) | 109.7(2) |
| O–Sn–C(61) | 85.5 | C(11)–P–C(31) | 105.8(3) |
| C(41)–Sn–C(51) | 119.0(2) | C(21)–P–C(31) | 108.9(3) |
| C(41)–Sn–C(61) | 117.4 | | |
| | | | |
| Sn–C(41)–C(42A) | 121.9 | Sn–C(41)–C(42B) | 122.0 |
| Sn–C(41)–C(45A) | 125.0 | Sn–C(41)–C(45B) | 125.3 |
| C(42A)–C(41)–C(45A) | 112.9 | C(42B)–C(41)–C(45B) | 112.1 |
| C(41)–C(42A)–S(43A) | 109.1 | C(41)–C(42B)–S(43B) | 108.4 |
| C(42A)–S(43A)–C(44A) | 93.3 | C(42B)–S(43B)–C(44B) | 92.8 |
| S(43A)–C(44A)–C(45A) | 111.2 | S(43B)–C(44B)–C(45B) | 111.0 |
| C(41)–C(45A)–C(44A) | 111.9 | C(41)–C(45B)–C(44B) | 111.5 |
| Sn–C(51)–C(52) | 124.9(5) | | |
| Sn–C(51)–C(55) | 124.6(4) | | |
| C(52)–C(51)–C(55) | 110.4(5) | | |
| C(51)–C(52)–S(53) | 112.8(6) | | |
| C(52)–S(53)–C(54) | 92.5(4) | | |
| S(53)–C(54)–C(55) | 113.3(6) | | |
| C(51)–C(55)–C(54) | 110.9(6) | | |
| Sn–C(61)–C(62A) | 122.2 | Sn–C(61)–C(62B) | 121.6 |
| Sn–C(61)–C(65A) | 124.1 | Sn–C(61)–C(65B) | 125.7 |
| C(62A)–C(61)–C(65A) | 113.7 | C(62B)–C(61)–C(65B) | 109.3 |
| C(61)–C(62A)–S(63A) | 108.9 | C(61)–C(62B)–S(63B) | 109.3 |
| C(62A)–S(63A)–C(64A) | 93.8 | C(62B)–S(63B)–C(64B) | 88.4 |
| S(63A)–C(64A)–C(65A) | 111.2 | S(63B)–C(64B)–C(65B) | 110.5 |
| C(61)–C(65A)–C(64A) | 111.8 | C(61)–C(65B)–C(64B) | 110.9 |

| | *n* = 1 | *n* = 2 | *n* = 3 |
|---|---|---|---|
| P–C(*n*1)–C(*n*2) | 118.8(4) | 122.0(5) | 124.1(5) |
| P–C(*n*1)–C(*n*6) | 120.7(5) | 118.1(4) | 116.6(5) |
| C(*n*2)–C(*n*1)–C(*n*6) | 120.5(5) | 119.9(5) | 119.2(6) |
| C(*n*1)–C(*n*2)–C(*n*3) | 119.2(6) | 118.8(6) | 119.9(7) |
| C(*n*2)–C(*n*3)–C(*n*4) | 120.5(8) | 121.5(6) | 120.5(9) |
| C(*n*3)–C(*n*4)–C(*n*5) | 120.5(7) | 119.0(7) | 118.9(8) |
| C(*n*4)–C(*n*5)–C(*n*6) | 122.1(7) | 120.4(6) | 121.7(7) |
| C(*n*1)–C(*n*6)–C(*n*5) | 117.0(7) | 120.4(5) | 119.5(7) |

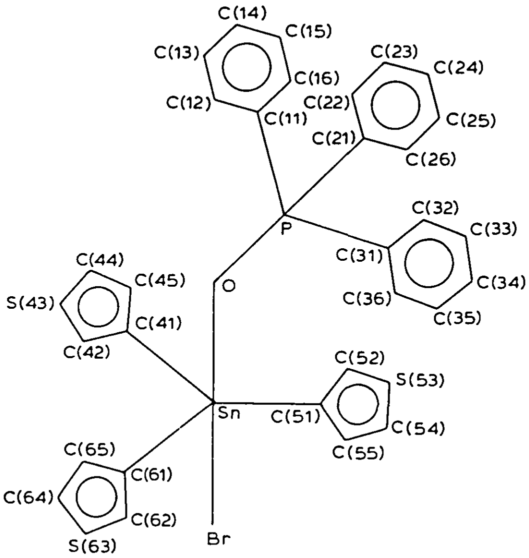

Fig. 1. Labelling scheme adopted for tri-3-thienyltin bromide·triphenylphosphine oxide. Two of the 3-thienyl groups are disordered with a common C(*n*1) (*n* = 4 or 6) atom and the remaining atoms designated A or B.

## Discussion

The TPPO adducts of triphenyltin halides have been predicted, on the basis of partial quadrupole splitting calculations [3,4], to have a trigonal bipyramidal structure with equatorial aryl groups. The observation of similar Mössbauer parameters for the related 3-thienyl compounds (Table 3) suggests that they also adopt a similar geometry. $^{119}$Sn NMR solution studies [5] are also indicative of an increase in coordination number for tin. The $^{119}$Sn NMR signal shifts to a considerably lower frequency for the adduct compared with the unassociated tin species.

TABLE 3

MÖSSBAUER DATA FOR TRI-3-THIENYL, TRIPHENYLTIN HALIDES AND THEIR TRIPHENYLPHOSPHINE OXIDE ADDUCTS

| | Isomer shift [a] $\delta$(mm s$^{-1}$ $\pm$0.02) | Quadrupole splitting $\Delta$ (mm s$^{-1}$ $\pm$0.02) |
|---|---|---|
| $Ph_3SnCl$ | 1.37 | 2.45 Ref. 13 |
| $Ph_3SnBr$ | 1.37 | 2.46 |
| $(3\text{-}C_4H_3S)_3SnCl$ | 1.21 | 2.29 |
| $(3\text{-}C_4H_3S)_3SnBr$ | 1.25 | 2.08 |
| $Ph_3SnCl \cdot Ph_3P{=}O$ | 1.28 | 3.23 Ref. 3 |
| $Ph_3SnBr \cdot Ph_3P{=}O$ | 1.29 | 3.20 Ref. 3 |
| $(3\text{-}C_4H_3S)_3SnCl \cdot Ph_3P{=}O$ | 1.18 | 3.08 |
| $(3\text{-}C_4H_3S)_3SnBr \cdot Ph_3P{=}O$ | 1.21 | 3.30 |

[a] Relative to $BaSnO_3$.

The present single crystal X-ray study confirms that the TPPO adduct of tri-3-thienyltin bromide does adopt a trigonal bipyramidal arrangement in the solid state, in which bromine and oxygen (TPPO) occupy axial positions, while the aryl groups are equatorial (Fig. 2). Although there is only a slight angular distortion from a regular trigonal bipyramidal arrangement, the bond angles do reveal that the tin atom lies out of the trigonal equatorial plane (0.182 Å), and in a direction towards the bromine atom. Thus the C–Sn–Br angles lie in the range 94.0–95.6°, while the C–Sn–O angles are significantly smaller, ranging from 84.3–85.5°. In general, the structure is reminiscent of an early $S_N2$-like transition state for substitution at tin.

The disordered 3-thienyl groups show an almost equal preference for the two possible sites with population parameters of 55 and 45%. The apparent ease with which these thienyl units may rotate about the Sn–C bond appears to be a consequence of the lack of any significant inter- and/or intra-molecular interactions involving the heteroaryl group. Rotational disorder of this type has previously been observed for 2-thienyl groups attached to tin [6]. Similar disorder has been found both for 3-thienyl and for 2-thienyl groups attached to phosphorus [7,8]. In contrast, the C(51), C(52), S(53), C(54), C(55) ligand is completely ordered and this may be a direct consequence of the close proximity of one of the phenyl groups (C(21)–C(26)), thereby inhibiting rotation about the Sn–C(51) bond.

The Sn–Br distance (2.651(1) Å) is increased relative to that found in the parent tri-3-thienyltin bromide molecule (2.49 Å), and is significantly longer than the sum of the covalent radii (2.54 Å). This would appear to reflect an increase in the coordination number of tin, from four to five. Similar lengthening of the tin–halogen bond has been observed for trimethyltin chloride on complexation with hexa-

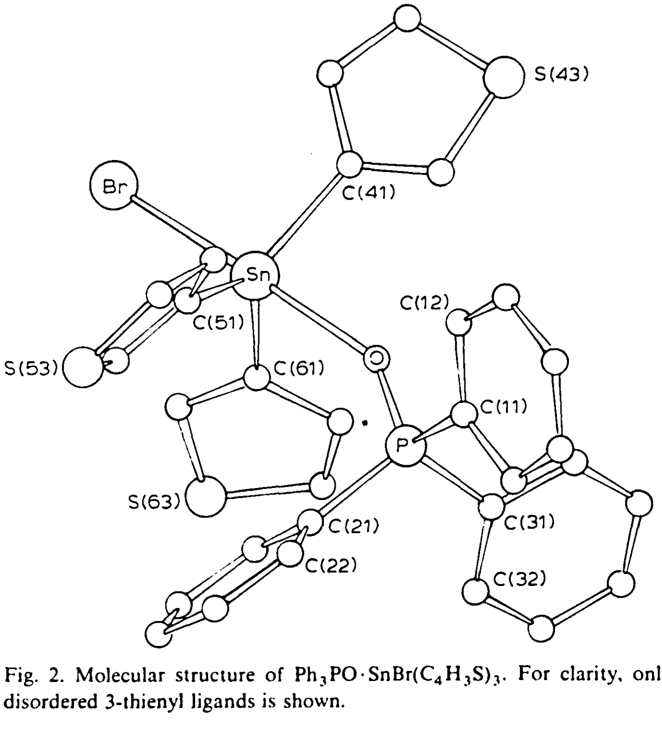

Fig. 2. Molecular structure of $Ph_3PO \cdot SnBr(C_4H_3S)_3$. For clarity, only one conformation of the two disordered 3-thienyl ligands is shown.

methyltriamido phosphate (from 2.36 to 2.52(2) Å [9]). The length of the Sn–O bond (2.335(4) Å), which is considerably greater than the sum of the covalent radii (2.13 Å), is also significantly longer than Sn–O distances reported for many tin complexes, including for example dimethylchlorotin acetate (shortest Sn–O 2.165(6) Å) [10] and $\mu$-bis(diphenylphosphinyl)ethane-bis(nitratotriphenyltin), Sn–O 2.220(5) Å [11]. It would appear that the tin–oxygen interaction in the present TPPO adduct is relatively weak and certainly the P–O distance shows only a slight lengthening upon coordination (from a mean value of 1.475 to 1.510(4) Å). The resulting P–O bond length is considerably shorter than the sum of the covalent radii (1.83 Å) and is indicative of the presence of substantial $\pi$-character. The coordination of the TPPO ligand is similar to that found in nitratotriphenyl (triphenylphosphine oxide)tin(IV) [12], where the Sn–O and P–O distances are 2.29(2) and 1.47(2) Å respectively. The Sn–O–P angle in this nitrato complex is 153(1)° and may be compared to that found in the present study (146.9(2)°).

## Acknowledgements

We wish to thank SERC for equipment grants (to IWN, JSB) and one of the authors (DJD) is indebted to the SERC and the International Tin Research Institute for a CASE award. We also thank Miss L.A. March for her assistance with the X-ray study.

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